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“Dynamics of Plasma-Surface Interactions using In-situ Ion Beam Analysis”

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Summary

The overall goal of this proposal was to develop an innovative experimental facility that would allow for the measurement of real-time response of a material surface to plasma bombardment by employing in-situ high-energy ion beam analysis. This facility was successfully developed and deployed at U. Wisconsin-Madison and was named DIONISOS (Dynamics of IONic Implantation & Sputtering on Surfaces).

There were several major highlights to the DIONISOS research which we will briefly highlight below. The full technical details of the DIONISOS development, deployment and research results are contained in the Appendices which contain several peer-reviewed publications and a PhD thesis devoted to DIONISOS. The DIONISOS results on deuterium retention in molybdenum were chosen as an invited talk at the 2008 International Conference on Plasma-Surface Interactions in Toledo, Spain.

Design Highlights

The DIONISOS design activity was significant. For the first time ever, a high power magnetized plasma environment was combine with high-energy ion beams from an accelerator. This posed several unique challenges that were overcome in the first 1.5 years of design and implementation.

1. The 1.7 MV tandem ion accelerator was refurbished and commissioned. The accelerator was re-assembled and installed at UW-Madison after being shipped from Bell Labs in New Jersey, from where it was purchased

2. A dedicated plasma exposure chamber was designed which featured several innovations (Fig. 1)
- A solenoid magnetic field up to 1 kGauss.
 - Port access for the ion beam through the field coils.
 - Changeable plasma source region in the solenoid field.
 - A plasma extraction chamber with ~12 diagnostic access ports for ion beam and plasma diagnostics.

Fig. 1 Schematic of the DIONISOS plasma experiment. The steerable high energy (MeV) ion beam produced by the tandem accelerator allows for in-situ, real-time ion beam analysis of material surfaces undergoing plasma bombardment.

3. A highly flexible material sample holder (Fig. 1) which included
- Push/pull temperature control up to 800 K
 - Target biasing up to 500 V to control plasma ion energy.
 - Capability to hold large-size samples 10x10 cm.
 - Beam alignment tools

4. Design of a helicon plasma source with a 3 kW 13.6 MHz RF source with digitally controlled particle and power flowthrough. Plasma densities up to $\sim 10^{19} \text{ m}^{-3}$ were achieved in argon.
5. Innovative charged-particle detectors for ion beam analysis that included active cooling and particle shielding from the nearby plasma. This allowed in-situ surface analysis when the plasma was bombarding the target samples.
6. Remotely controlled beam-steering and rastering across the sample face using upstream electrostatic deflectors and strong differential pumping.
7. Plasma diagnostics including a scanning langmuir probe and infrared thermography of the target.

In summary, the design was successful at integrating a high flux plasma exposure chamber with real-time in-situ ion beam surface analysis for the first time.

Research Highlights

The latter half of the research grant activity focused on deuterium fuel retention in refractory metals. In future burning plasma devices like ITER, tritium fuel retention is a serious safety concern; and tritium fuel economy is a concern for eventual fusion reactors breeding their own tritium. At the same time, refractory metals such as molybdenum and tungsten are leading candidates as PFC materials because of their erosion resistance. We used the unique scientific measurement tools of DIONISOS to explore the dynamic interaction of a deuterium plasma with the metals to illuminate fundamental process of importance. Further motivation was provided by measurements of high D retention in Mo tiles in Alcator C-Mod, which prompted us to perform most of the experiments in pure Mo.

1. A unique method to obtain real-time D depth profiles during plasma operation with a 3-Helium ion beam was developed (Fig. 3). Typically He ion beam energy is changed to provide depth resolution using Nuclear Reaction Analysis; however this is not possible if one desires good time resolution. Rather we developed methods to interpret the energy spectrum of the high-energy protons produced by the nuclear reaction (3He on D) which provided ~ 200 nm depth resolution.
2. Real-time measurements of D in the Mo showed a dynamic response of the surface to the plasma bombardment (Fig. 4). A large surface concentration, $\sim 1\%$ D/ Mo atom would appear instantaneously with the plasma ion bombardment and promptly disappear with its removal. This was shown to be consistent with surface recombination limiting the release of D under high flux. The surface concentration of D has always previously been inferred from permeation

Fig. 3 Examples of ion beam surface analysis. (a) Ex-situ proton RBS spectrum of a boron-coated Mo tile from C-Mod (b) Fitted depth distribution of boron and molybdenum mixed layers (c) In-situ Deuterium depth profiles in Mo at various exposure times to D plasma in DIONISOS using

measurements. The direct measure of mobile D with plasma showed those to under-estimate the surface D concentration; which is a critical parameters for setting permeation time of the D through the metal. Alcator C-Mod experiments comparing D and He (which does not recombine) plasmas confirmed the importance of recombination in setting D retention.

Fig. 4 Dynamic response of molybdenum D fuel retention to DIONISOS plasma. NRA-measured D profiles (inset) reveal dynamically increased D concentration near the surface, as well as the evolution of long-term D retention.

3. Varying the Mo temperature was shown to be the most critical parameter in setting the retained D, rather than plasma energy. This confirmed that permeation and trapping processes were dominating the retention. Real-time depth profiles showed that the retention moved from being dominated by diffusion near room temperature to being dominated by trap densities at elevated temperatures ($> 500 \text{ K}$). The concentration of D/Mo was found to reach $\sim 1\%$ in many cases, a level much higher than expected from “pure” Mo properties. It was ascertained that the plasma exposure itself was causing damage sites at which the D could then be trapped and retained. This observation of $1\% \text{ D/MO}$ and plasma-caused traps was found to be consistent with C-mod retention results. However the exact damage mechanism in this case was unresolved.

4. Displacement damage was found to play a critical role in increasing the ability of the Mo to retain D. The effect of neutron damage in ITER or a reactor will cause large relative displacements per atom. This effect was simulated in DIONISOS using the 3.5 MeV helium ion beam to cause displacement through the first 10 microns of the material. The displacement has a dramatic effect on D retention, increasing the total D inventory by up to a factor of 10 in the Mo. This was identified as a previously overlooked phenomenon in ITER that could enhance the retention of tritium in tungsten. As a result of this work, further studies and calculations were implemented which showed that this effect could strongly increase the tritium retention in ITER through its lifetime.
5. A numerical model was developed to interpret the results and uncover the physical mechanisms controlling the D-Mo retention results. This included real-time D profiles during high temperature annealing of the samples after plasma exposure. Taken together with the D profiles during and after plasma bombardment, the DIONISOS data provided unique data to constrain the modeling of the solute and trapped D. Fundamental properties such as the D diffusion rates in Mo were independently determined and compared favorably with literature. Furthermore, trap mobility and de-trapping of D were also determined. These results showed that the damage sites were finding means to effectively migrate through the material; a result of prime importance to explain the high levels of D retained.
6. The role of surface impurities was examined by combining D measurements in Mo with low-Z surface contamination measurements with NRA. It was shown in tiles exposed to C-Mod that the surface boron (from boronizations) could strongly impact the migration of the D into and through the surface, and therefore strongly affect retention. This was consistent with the observations of low retention in B-covered Mo in Alcator C-Mod.

In summary, despite a relatively simple plasma-material interaction (D on pure Mo) the unique and new diagnostic capabilities of DIONISOS yielded a surprisingly rich set of phenomena. The results of DIONISOS were shown to be consistent with results from confinement devices like C-Mod and even inspired more experiments on the tokamaks.

Furthermore the DIONISOS results were instrumental in uncovering several important aspects of tritium retention in tungsten for application in ITER.

Appendix 1

Dynamics of hydrogenic retention in molybdenum: First results from DIONISOS

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Abstract

The DIONISOS (Dynamics of ION Implantation and Sputtering of Surfaces) experiment is described. DIONISOS features steady-state plasma exposure of material surfaces, with simultaneous, in situ, non-destructive depth profiling on the same surfaces with ion beam analysis (IBA). A steady-state RF helicon plasma source produces a fusion ‘edge-like’ low temperature ($T \sim 1\text{--}10\text{ eV}$), high-density ($\leq 10^{17\text{--}18}\text{ m}^{-3}$), steady-state, cylindrical, plasma ($\phi \sim 50\text{ mm}$). The exposure stage allows for the control of sample surface temperature (300–800 K), incident ion energy (10–500 eV), and ion beam and magnetic field incident angle (360° rotation), during bombardment with high plasma flux ($\sim 10^{20}\text{--}10^{22}\text{ s}^{-1}\text{ m}^{-2}$). First results from DIONISOS show a large and evolving concentration of deuterium ($\sim 1000\text{ appm}$) trapped deep ($\sim 5\text{ }\mu\text{m}$) in molybdenum. IBA during plasma exposures shows the surface dynamic deuterium inventory increased by a factor of 2 over the ‘long-term’ trapped inventory at an incident ion flux density of $\sim 1.5 \times 10^{21}\text{ D/m}^2\text{ s}$.

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1. Introduction

As experiments move towards longer discharges and to time scales at which thermal equilibrium can be obtained at the wall, a concern is how dynamic plasma–surface interactions will affect plasma operation, material lifetimes and tritium fuel retention. For example, a recent study of the fuel inventories and particle control during long-pulse

discharges in JT-60U concluded that dynamic retention dominated the carbon wall fuel inventories [1]. The dynamic interplay between surfaces and the plasma should be expected in a fusion device given the high level of recycling and the sensitivity of the plasma behavior to impurities from wall erosion. For a long-pulse device that achieves quasi plasma–surface equilibrium, small changes in material properties (e.g. dynamic fuel retention rate) could strongly affect particle and performance control in a long-pulse discharge [2]. Unfortunately, the underlying cause of these dynamics must be inferred from plasma behavior, while the underlying

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mechanism that controls the dynamics is actually the evolution of materials properties. Direct measurements of such material evolution are extremely difficult in a fusion device, due to the limitations of in situ plasma–surface interaction diagnostics. As more attention is focused on physics of long-pulse plasma discharges, such as for ITER, the demand to examine the dynamics of plasma–surface interactions increases.

The DIONISOS (Dynamics of ION Implantation and Sputtering Of Surfaces) experiment was designed to address these issues. The DIONISOS experiment probes the surface of a specimen using in situ ion beam analysis techniques while simultaneously exposing that same surface to a low temperature, high density, fusion ‘edge-like’ plasma. This allows for spatially and depth-resolved measurements of fuel inventory and material erosion/deposition, before, during, and after plasma exposure.

The focus of this article is two-fold: to describe the design and abilities of DIONISOS and to report its first results with regard to the dynamic and long-term retention of deuterium (D) fuel in molybdenum (Mo). High D retention rates seen recently in the Mo-clad Alcator C-Mod [3] substantially exceed retention rates measured in laboratory experiments [4–10]. These results, and the general interest in refractory metals for fusion (e.g. W in ITER), motivated these first experiments. Molybdenum specimens were taken from Alcator C-Mod and exposed at the PISCES-A experiment [11]. These specimens were analyzed with ex situ NRA, elastic recoil detection (ERD), and thermal desorption spectroscopy (TDS). The results from the PISCES-A exposures were used to scope exposure conditions for DIONISOS. Molybdenum plates and foils were exposed to a range of plasma fluence and flux densities in DIONISOS. Depth-resolved deuterium concentrations were made with in situ ^3He nuclear reaction analysis (NRA). The ability to directly measure dynamic retention allows us to infer underlying surface processes such as deuterium diffusion, trapping and surface recombination, which can eventually be applied to tokamak situations.

2. Experiment

2.1. The DIONISOS experiment

The DIONISOS experiment is designed to allow simultaneous plasma exposure and ion beam analysis (IBA) of a sample surface. To achieve this, a heli-

con plasma exposure chamber was mounted on the end of a 1.7 MeV tandem ion accelerator beam line (see Fig. 1). DIONISOS is comprised of three main components: the exposure chamber (vacuum vessel, sample holder, cooling system, etc.), the helicon plasma source, and the ion accelerator used as the main diagnostic for the experiment.

The DIONISOS facility is designed to provide abundant diagnostic and physical access to the specimen surface and to recreate a large range of surface conditions for plasma exposures. The DIONISOS vacuum vessel is a custom-built chamber with 19 diagnostic ports, 5 of those being line-of-sight ports onto the sample surface. A hinged door on the back of the vessel allows for easy access to the interior of the chamber and the sample holder. This allows for quick change of samples although vacuum must be broken to do so. Vacuum of $\sim 10^{-6}$ Pa has been achieved, although typical vacuum tends to be closer to $\sim 10^{-5}$ Pa.

The DIONISOS sample holder can recreate a large range of surface conditions while maintaining flexible attachment for a large variety of sample shapes and sizes. Samples are mounted to a $10\text{ cm} \times 9\text{ cm}$ copper plate heat sink suspended in the vessel from above. The only shape requirement is that good mechanical and thermal contact to the flat copper heat sink can be obtained. The sample holder is mounted on a 360° rotatable platform, which allows for a full control over the incident angle of the ion beam or axial magnetic field (although the angle between the field and ion beam is fixed at 45°). The heat sink has both water and air cooling capabilities and active heating for temperature control ranging from 300 to 800 K using a feedback control with thermocouples and resistive temperature devices (RTD). Surface temperature can also be monitored with infrared imaging. The sample holder is electrically floating with respect to the chamber walls, which allows the sample to be actively biased up to 600 V, thus controlling incident ion energy. The entire heat sink can be removed for maintenance or to be replaced with another custom heat sink for samples of inconvenient shape (rods, spheres, etc.).

The DIONISOS plasma source is an RF helicon plasma supply. The helicon mode provides high density and low temperature plasmas for an RF source. The source consists of an $m = 1$ Nagoya type III antenna surrounding a cylindrical quartz tube. The antenna is attached to a 5 kW RF power supply through a manual match network. Typical

Fig. 1. A schematic of the DIONISOS experiment.

helicon plasmas have $<5\%$ reflected power. Plasma parameters are measured by a scanning Langmuir probe in the exposure chamber ~ 10 cm from the target. Deuterium plasma flux density and electron temperature have been measured across the plasma column (e.g. Fig. 2). The plasma flux density follows a Gaussian curve peaked at the center of the column. This Gaussian shape has been confirmed by IR thermography of the plasma footprint. The Gaussian shape of the flux density provides the ability to measure the effects of various plasma flux densities by simply re-steering the ion beam to analyze different radial locations within the column. The electron temperature profile is fairly flat across the plasma column ranging from 4 to 6 eV. The quartz tube and DIONISOS chamber are surrounded by a set of four Helmholtz coils with a maximum axial magnetic field of ~ 1 kG. The plasma is confined by the magnetic field and extracted from the source resulting in a cylindrical plasma on target. Neutral gas is fed into the back of the quartz tube and gas flow is controlled by a mass flow controller. Neutral gas pressure inside the vacuum vessel is measured by a capacitance manometer during plasma operations. Typical neutral pressures for deuterium plasmas are ~ 0.3 – 1 Pa.

A 1.7 MV Pelletron tandem ion accelerator is used to produce ion beams for IBA of sample surfaces. The ion accelerator provides ions with ener-

Fig. 2. The (a) ion flux density and (b) electron temperature as a function of plasma radius. Measurements were taken ~ 10 cm from the target plate for a deuterium plasma with $B = 500$ G, $P_{\text{RF}} = 500$ W, and $p_{\text{D}} = 0.8$ Pa.

gies of ≤ 10 MeV. An energy feedback loop keeps the beam monoenergetic to within ~ 1 keV. Ion

beam currents of 100's μA can be achieved, but typical beam currents for surface analysis are 0.5–3 μA to ensure that they are not perturbing the surface. The beam spot can be magnetically focused on the target to a spot diameter of $\sim 2\text{ mm}$. Magnets and electrostatic steerer plates are also used to move the beam spot both horizontally and vertically across a sample surface. DIONISOS has no limiting apertures so that all locations on the target are accessible to the ion beam. Horizontal and vertical control of a very tight beam spot allows for detailed spatial scans of material surfaces, e.g. radial erosion/deposition profiles as might be found near a divertor strikepoint.

Most standard IBA techniques are available on DIONISOS: nuclear reaction analysis (NRA), particle-induced gamma emission (PIGE), elastic recoil detection (ERD), and Rutherford backscattering (RBS). Solid-state charged particle detectors are used to detect reaction products or scattered particles. The data acquired by the solid-state detectors is fit using the SIMNRA simulation [12], yielding a non-destructive depth-resolved layer structure of the elemental composition of the surface. The ion beam is checked to be non-perturbing since repeated IBA on the same spot yield the same spectra.

During simultaneous IBA and plasma exposure of a surface, the large energy gap between beam ions and plasma ions allows these ions to act independently of one another. The stopping distance for a beam ion in the exposure chamber plasma ($n_{\text{gas}} < 10^{20}\text{ m}^{-3}$) is $>10^3\text{ m}$, so there is little to no interaction. However, atoms sputtered off the sample surface with $E \sim \text{eV}$ will have a mean free path of $\sim \text{cm}$, i.e. the sputtered particle can be ionized and re-deposited before escaping the plasma column, similar to recycling in a tokamak. The axial magnetic field used for the helicon plasma source can deflect the incident ion beam. However, since the beam can be visually aligned with the field on, any deflection (typically $\leq 1\text{ cm}$ for most ion beam and magnetic field combinations) can be compensated for with electrostatic steering plates.

2.2. Molybdenum samples

Two types of Mo samples were exposed in DIONISOS, a polycrystalline $10\text{ cm} \times 10\text{ cm} \times 1.6\text{ mm}$ 99.97% Mo plate from Ed Fagan Inc. and a polycrystalline $10\text{ cm} \times 10\text{ cm} \times 25\text{ }\mu\text{m}$ 99.99% Mo foil from Elmet Technologies. Both samples were cleaned with alcohol before exposure but no

other sample preparation was performed on either sample.

The plasma exposure conditions for the Mo plate were $E_D = 100\text{ eV}$, $T_e \sim 5\text{ eV}$ with a peak ion flux density of $\sigma_D = 1.8 \times 10^{21}\text{ D/m}^2\text{ s}$. The Mo plate was actively water cooled during plasma exposure and the sample temperature was measured to be $\leq 310\text{ K}$. For the Mo foil, plasma parameters were $E_D = 100\text{ eV}$, $T_e \sim 5\text{ eV}$ with a peak ion flux density of $\sigma_D = 8 \times 10^{20}\text{ D/m}^2\text{ s}$. The Mo foil was actively water cooled, but due to poorer thermal contact with the heat sink, the surface was heated to $\sim 400\text{ K}$ by the plasma. Once the plasma was removed, the surface temperature returned to $\sim 300\text{ K}$ in $<10\text{ s}$.

An incident ion beam of $3.5\text{ MeV } ^3\text{He}^{++}$ was used to detect deuterium up to $\sim 5\text{ }\mu\text{m}$ into the surface using the $^3\text{He(d,p)}^4\text{He}$ nuclear reaction.

3. Results and discussion

3.1. 25 μm Mo foil at 370 K

A fluence scan was performed on the Mo foil at 400 K (see Fig. 3) at the center of the plasma column. The deuterium concentrations were obtained in situ $\sim 100\text{ s}$ after plasma exposure, but with no plasma present on the sample. After a fluence of $2.5 \times 10^{23}\text{ D/m}^2$, the deuterium already appears at depths $>1\text{ }\mu\text{m}$, and at high concentrations ($\sim 3500\text{ appm}$) near the surface. As the fluence increases, the deuterium moves deeper into the sample until at a fluence of $1.7 \times 10^{24}\text{ D/m}^2$ the deuterium extends past the maximum detection depth, $\sim 5\text{ }\mu\text{m}$, of the $3.5\text{ MeV } ^3\text{He}$ ions. The deuterium concentration at all depths increases with incident fluence showing no signs of

Fig. 3. Depth profiles of the trapped D concentration in the $25\text{ }\mu\text{m}$ Mo foil for four different ion fluences (taken after plasma exposure). These measurements were performed at the center of the plasma-exposed area.

local saturation. At the maximum fluence of 1.7×10^{24} D/m², the concentration of deuterium at the surface is ~ 8000 appm.

At an ion energy of 100 eV/D⁺, there are no vacancies produced in the Mo by the deuterium (nor sputtering of Mo). However, evolving trapped deuterium concentrations up to ~ 8000 appm indicate trap production in the surface region. The mechanism of this inferred trap production is unknown and requires further study. One possibility is pressure-induced trap production due to the high flux of implantation at low energies, similar to void or blister formation [13,14]. Depth profiles of 10 keV D⁺ implanted in Mo were measured by Nagata et al. [7]. For a fluence of $\sim 1 \times 10^{22}$ D/m² at 346 K, the deuterium was detected at depths up to 4 μ m but the concentration in the first micron of the surface was reduced as compared to a 298 K exposure. In the exposures on DIONISOS, the concentration at the surface continues to rise as the trapped deuterium appears to diffuse into the bulk. This discrepancy may be due to the higher flux densities achieved in DIONISOS ($\sim 1 \times 10^{21}$ D/m² s) than by Nagata et al. ($\sim 1 \times 10^{18}$ D/m² s), allowing for a greater fraction of surface traps to be occupied before the implanted D can diffuse into the bulk. The high ion energies (10 keV/D) used by Nagata et al. as opposed to the much lower DIONISOS ion energies (100 eV/D) may also be playing a role in terms of trap production.

Since the deuterium is detected much deeper than the implantation range of 100 eV D⁺ in Mo (~ 2 nm), it is clear that the trapped deuterium is migrating further away from the implantation zone. The total plasma fluence was obtained over an exposure time of ~ 2100 s. Taking measured deuterium diffusion rates in Mo [15–18] and extrapolating the fits to $T = 400$ K, the diffusion length scales associated with a time scale of 2100 s range from 3.5 to 1400 μ m. Because of the large scatter of measured deuterium diffusion rates in Mo, it is unclear if the diffusion that is occurring in the Mo foil is deuterium diffusing through Mo or *trap sites* diffusing from the surface into the bulk of the sample. Whatever the cause, it is clear that the plasma exposure itself is evolving the trapped deuterium profiles in the Mo.

3.2. 1.6 mm thick Mo plate at 300 K

Both the dynamic (with plasma on) and trapped (plasma off) inventories were measured for the Mo

Fig. 4. NRA measured retained D fluence in the Mo plate in real-time; before, during, and after a deuterium plasma exposure with flux density of 1.8×10^{21} D/m² s and $V_{\text{bias}} = 100$ V.

plate in DIONISOS (Fig. 4). The Mo plate was previously exposed to deuterium plasmas, which is why the initial retained fluence is not zero. The inventories were determined by integrating the measured deuterium concentration profile over the entire detection depth.

It is clear that the presence of the plasma has an immediate effect on the deuterium inventory. In the presence of the plasma, the deuterium inventory increases by $\sim 50\%$ but continues to evolve and increase with passing time. NRA shows that the dynamically stored D is in the first 500 nm of the surface. By the end of the exposure, the dynamic inventory is a factor of 2–3 greater than the pre-exposure inventory. This continuing evolution of the dynamic inventory may be another indication of trap production in the implantation zone by low-energy, high flux plasmas.

Once the plasma is removed, the Mo plate no longer has a source of ions into its surface. The deuterium inventory evolves as the implanted, but non-trapped, deuterium is released from the surface. The deuterium inventory decays to a steady-state inventory that is representative of trapped deuterium. The asymptotic trapped deuterium inventory is $\sim 25\%$ greater than the pre-exposure inventory, indicating long-term trapping.

The dynamic inventory enhancement is a factor of 2 greater than the increase in the trapped inventory. Previous dynamic inventory measurements made on carbon by Emmoth et al. [19] also show an enhanced dynamic inventory in carbon. Initial results on Mo indicate that the dynamic inventory increases as the square-root of incident flux density (obtained by NRA on different radial locations). The square-root dependence is consistent with the surface recombination limiting the deuterium release as molecules assuming the recombination

Fig. 5. A comparison of D retention results obtained on the DIONISOS experiment with results from wall-pumping experiments on Alcator C-Mod [3] and ex situ analysis of Mo exposed at PISCES-A. The PISCES-A samples were thermally desorbed at 1300 K before exposure.

sites are not saturated [20]. The post-exposure inventory decreases with ~ 500 s e-folding time. The deuterium inventory reaches equilibrium, showing that the ion beam is non-perturbing in this case.

Overall retention rates (scaled to incident ion fluence) from the DIONISOS experiment (to-date) are compared to the observed retention rates in Alcator C-Mod results from ex situ analysis of Mo exposed in PISCES-A (see Fig. 5). As with C-Mod, no sign of D retention saturation is found. The retention magnitude from DIONISOS is larger than seen with ex situ analysis. The PISCES-A samples were thermally desorbed at 1300 K for ~ 600 s before plasma exposure. This thermal desorption may have an annealing effect on the sample and reduce the retention rates in subsequent exposures [21]. The DIONISOS results are ~ 5 – 10 times smaller than found for C-Mod. This requires further study.

4. Conclusions

Deuterium implanted into Mo with a low energy, high flux plasma can be found at depths in excess of $5 \mu\text{m}$. The maximum deuterium concentration found in the surface region was ~ 8000 appm although there were no indications that this was a saturation level, so concentrations may continue to increase with increasing fluence. There is also strong evidence of trap production in the surface region by exposure to a low-E, high flux plasma. No mechanism has been confirmed for this trap production. Overall retention linearly increases with fluence at 400 K, $\sim 0.05\%$ retained per incident

ion, although this is still smaller than inferred from C-Mod experiments.

Measurements of the dynamic inventory of deuterium in Mo show that the dynamic inventory is enhanced over the trapped inventory by a factor of 2–3. Early results also indicate the dynamic inventory scales as the square-root of incident flux, consistent with surface recombination limiting D molecular release.

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Appendix 2

Measurement of hydrogenic retention and release in molybdenum with the DIONISOS experiment

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ABSTRACT

Molybdenum targets are exposed in the DIONISOS experiment to a deuterium (D) plasma ($\Gamma_D \sim 10^{21} \text{ m}^{-2} \text{ s}^{-1}$) at target biases of 30–350 V and target temperatures of 300–700 K while simultaneously diagnosing the D in the surface with a 3.5 MeV ^3He ion beam. The ^3He diagnostic beam creates displacements in the Mo lattice which can then trap D, allowing retention far beyond the plasma ion implantation range. The conversion of displacements to trap sites averaged over the ion range is non-linear with a scaling $(\text{dpa})^\alpha$, $0.25 \leq \alpha \leq 0.5$. The beam-induced traps are distributed from the surface to the end of range as opposed to the damage (dpa) profile that is concentrated at the end of range. Measurement of the near-surface D time-dependence has allowed inference of an effective surface recombination rate, which is lower than predicted by theory and at the low end of those found in literature.

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1. Introduction

Molybdenum (Mo) is used in several tokamaks (e.g. Alcator C-Mod, TRIAM, FTU) as a plasma-facing component (PFC) material due to its beneficial thermal properties and machinability as compared to tungsten (W). Also like W, both the solubility and inherent trap (sites for H to reside in the material) concentration are very low. It is expected that the hydrogenic retention in Mo will be low. Laboratory results for hydrogenic retention in Mo [1–5] show a low rate of retention when Mo is exposed to H or D ions. However the hydrogenic retention for Mo in a tokamak environment is not well documented. For example, a campaign in Alcator C-Mod was performed with bare Mo PFC (10–15 at.% B on the surface of most tiles). For 10 dedicated discharges, the D retention increased linearly at roughly 1% of incident ion fluence [6,7]. Both the absolute rate of this D retention and the lack of saturation in the Mo PFCs are unexpected. In addition, the hydrogenic retention in a nuclear environment is also not well understood or documented. This becomes a more pertinent and urgent issue as we move towards power producing devices operating in a neutron environment.

The DIONISOS experiment simultaneously exposes the target to a plasma flux and an irradiating MeV ion beam, the latter used for simultaneous analysis of the D content in the sample [8]. This configuration also allows the influence of the plasma and the irradiating ion beam on the hydrogenic retention properties of the Mo

targets to be measured independently and synergistically. DIONISOS thus yields insights into how D retention evolves throughout a plasma exposure rather than relying on post-mortem analysis. This reveals insights into the production of trap sites due to material irradiation by MeV-energy ions. The rate of trap production due to the ^3He ion beam is related to the rate of lattice damage as measured by displacements per atom (dpa) caused by the impact of the MeV-energy ions.

2. Experiment

The DIONISOS experiment exposes the target to a plasma produced by a helicon RF plasma source, while simultaneously irradiating the surface with a high-energy ion beam produced by a 1.7 MV Pelletron tandem ion accelerator (Fig. 1). In these experiments a 3.5 MeV $^3\text{He}^{++}$ beam was used to monitor the D content of the targets with nuclear reaction analysis (NRA) exploiting the $^3\text{He}(\text{d},\text{p})\alpha$ nuclear reaction. Further details on the DIONISOS experiment can be found elsewhere [8]. The 3.5 MeV $^3\text{He}^{++}$ ions impact the Mo target surfaces at an incident angle of 45° and a scattering angle to the detector of 90° . The typical ion beam spot was circular with a diameter of $\sim 5 \text{ mm}$. The typical ion beam current for the ^3He beam was $\sim 1.7 \mu\text{A}$ for $^3\text{He}^{++}$ (0.086 A/m^2). Table 1 lists the beam specifications for each exposure condition utilized in this paper.

The aim of the DIONISOS experiment is to investigate the dynamics of hydrogenic retention by tracking D depth profiles as a function of time. This makes the common method of achieving depth profiles, obtaining energy spectra for several ^3He ion ener-

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Fig. 1. A schematic drawing of the DIONISOS experiment.

gies [9], unfeasible due to time required to vary the beam energy and collect the data.

For DIONISOS, the D depth profile is obtained using a single ^3He energy. Normally a reliable depth profile is not feasible since the solid state detector has a large solid angle and the angular vs. energy distribution becomes convoluted. However, in DIONISOS, the detector is far (~ 35 cm) removed from the target (to avoid plasma heating) and thus subtends a much smaller solid angle and improves depth resolution of the D profile. The 90° scattering angle for the NRA measurements also helps to broaden the overall energy spectrum and reduce the effect of finite detector energy resolution. The ^3He NRA spectra are transformed into D concentration depth profiles using the simNRA program [10,11]. Discrete D and Mo layers in the simulation program produce discrete Gaussian peaks at known energies, based on the depth in the target (Fig. 2). Simulated layers of 500 nm were typically used for the fits in this investigation. Fits began with data from exposures at 300 K where, from the narrow peak in the measured energy spectrum, the D is clearly limited to the first micron. This established the leading edges of the Gaussian curves corresponding to the first micron. For higher target temperatures, as the measured energy spectrum broadened the deeper layers in simNRA were filled in and the surface layer adjusted in magnitude to match the leading edge of the measured spectrum. With He^3 beam currents of ~ 1.5 μA , spectrum acquisition times (time resolution) can be reduced to 250 s with $<10\%$ statistical uncertainties and D sensitivity of ~ 10 apm.

In these experiments, data was taken at negative target biases of 30, 100, and 350 V with Mo temperatures ranging from 300 to 700 K (see Table 1). The target bias sets the incident ion energies

Fig. 2. The Gaussian peaks produced by simNRA for DIONISOS geometry from a series of discrete, 1 μm layers with a concentration of 0.01 D/Mo. The magnitudes of the peaks are determined by the D/Mo ratio in the layer and the energy dependence of the reaction cross-section.

since the electron temperature, T_e , is measured to be 5 ± 1 eV. For the plasma exposures at a constant Mo temperature, the plasma flux density was kept at $1.0 \pm 0.1 \times 10^{21}$ D/m 2 s as measured by a Langmuir probe for all data sets except for the data set at 100 V. For those experiments, the flux density was measured to be $1.5 \pm 0.1 \times 10^{21}$ D/m 2 s (reflection not included). In all cases the to-

Fig. 3. (a) The measured D retention in the first 5 μm of the ^3He -irradiated Mo targets for the various target biases and (b) the corresponding D concentration depth profiles for Mo temperatures ranging from 300 to 700 K at target bias of 30 V. There was no significant variation in profiles due to variations in the target bias.

Table 1

Exposure conditions for Mo targets with voltage biases of 30, 100, and 350 V. The temperature scan is performed in steps of 100 K.

	Target bias		
	30 V	100 V	350 V
Mo Temperature range (K)	300–700	300–700	300–700
Plasma flux density (D/m 2 s)	1.0×10^{21}	1.5×10^{21}	1.0×10^{21}
$^3\text{He}^{++}$ beam current density (A/m 2)	0.086	0.050	0.086
Exposure time (s)	1500	1000	1500
Plasma fluence (D/m 2)	1.5×10^{24}	1.5×10^{24}	1.5×10^{24}
3.5 MeV $^3\text{He}^{++}$ fluence ($^3\text{He}/\text{m}^2$)	4.0×10^{20}	1.6×10^{20}	4.0×10^{20}

Fig. 4. D depth profiles at various times during a plasma exposure with the ^3He ion beam present. Results correspond to the 400 K curve in Fig. 3(b).

tal fluence was kept constant at 1.5×10^{24} D/m 2 , corresponding to an exposure time of 1500 or 1000 s depending on the plasma flux density.

The temperature of the target was measured with an ungrounded resistive temperature device (RTD). The surface of the target was also monitored with an infrared camera to ensure there was no deviation from the target temperature due to local heating by the ion beam or plasma. The Mo targets were 99.97% pure Mo plates purchased from Ed Fagan Inc. The targets used in this investigation were purchased in two separate batches. The first batch was used to determine the retention as a function of target temperature and bias (Sections 3.1 and 3.2, Fig. 3) and the second batch was used to determine the influence of the irradiating beam (Section 3.3, Figs. 5 and 6). The targets were exposed in the as received condition with no surface preparation other than cleaning with methanol and a bake at 400 K for ~ 30 min prior to exposure. Surface roughness was measured to be ~ 200 nm by interferometry.

3. Results

3.1. D retention as a function of surface temperature and target bias

The results for the total D retention in the first 5 μm (limit of NRA measurement depth) of the surface post-exposure can be seen in Fig. 3(a). The exposure conditions for these targets can be found in Table 1. We note that for real-time D detection the ^3He ion beam was irradiating the target throughout these plasma exposures which we will show later has a strong effect on retention. A single target specimen was used for all temperatures for a single target bias. After each plasma exposure the D was thermally desorbed at 750 K until the D concentration, as measured with in-situ with NRA, was <50 appm within the top 5 μm . Since the same specimens were used for all temperatures (but only a single target bias) this introduces the possibility of a history effect. However tests with repeated exposures found these effects to be small, presumably due to the long bake times between exposures. Since the same procedures and sequences were followed for all specimens, any history effects should be minimized for comparative purposes.

The total retention in the first 5 μm increases as the Mo temperature increases from 300 K to 400–500 K (Fig. 3(a)). The corresponding depth profiles of D concentration for the 30 V case are shown for all sample temperatures in Fig. 3(b). There was no significant variation in the D depth profiles due to variations in the target bias. The 600 K and 700 K profiles show a flat or close-to-flat deuterium profile indicating very deep penetration of the D into the surface and/or greater loss of D out the front surface. Since

Fig. 5. (a) Comparison of D depth profiles with and without the ^3He ion beam present to a plasma fluence of 1.5×10^{24} D/m 2 and an ion beam fluence of 4.4×10^{20} $^3\text{He}/\text{m}^2$. (b) The damage distribution (dpa) and ^3He ion implantation range for the exposure with the ^3He ion beam present. The traps/dpa curve is calculated from the difference from the curves in (a) and dividing by dpa curve in (b).

the deuterium concentration is non-zero at the end of detection range (5 μm) for intermediate (400–500 K) and high temperatures (600–700 K), it is possible there is deuterium trapped deeper than 5 μm in the Mo, meaning the retention values shown in Fig. 3(a) would be minimum retention values for these temperatures. This would imply that the lowest retention occurs at 300 K, which is counter to previous results [2,3].

Fig. 6. The trap density in the first 5 μm of the Mo surface, as measured by NRA detection of trapped D atoms, as a function of the total 3.5 MeV $^3\text{He}^{++}$ fluence. Measurements were taken at $T_{\text{Mo}} = 500$ K and $V_{\text{bias}} = 100$ V. The zero and maximum (4.4×10^{20} $^3\text{He}/\text{m}^2$) ^3He fluence cases correspond to the curves in Fig. 5(b).

TRIM [12] simulations show that at a 350 V target bias, incident D ions begin to create atomic displacements in Mo (assuming a 30 eV lattice binding energy). At target biases of 100 V, common plasma impurities such as carbon and oxygen are capable of creating displacements in the Mo surface although D ions cannot. At target biases below 50 V, neither the D ions nor plasma impurities are capable of creating displacements in the Mo lattice. Since the D retention is approximately equivalent for all these target biases, it follows that vacancies caused by the primary knock-ons of plasma ions are not a dominant trap source in the Mo for these experiments. The lack of retention-dependence on target bias also demonstrates that retention is weakly driven by the implantation range of the plasma ions.

3.2. Dynamics and role of diffusion in D retention

The depth profiles show that diffusion is playing an important role at lower T. The 300 K profile (Fig. 3(b)) appears to be diffusion-limited, but show D concentrations near the surface on the order of 1 at.% (i.e. much higher than any intrinsic trap density or hydrogenic solubility for Mo at low ambient pressure). The 400 K and 500 K profiles show a deuterium gradient away from the surface and the D begins populating trap sites deep ($>4\ \mu\text{m}$) in the material. Exploiting the unique DIONISOS ability to measure the time evolution of the D depth profile, at 400 K we can see a “leading edge” of implanted D diffusing deeper into the bulk as the plasma exposure proceeds (Fig. 4). At the end of the 1500 s plasma exposure, the implanted D has just reached the end of the ^3He ion range (5 μm). This is consistent with calculations using the diffusion rate from Tanabe [13], which shows that diffusion across 5 μm in 1500 s is possible for $T_{\text{Mo}} \geq 400\ \text{K}$ and that the retention in the 300 K case is diffusion-limited.

It is also important to understand the state of the D in the Mo, in particular the energy wells in which they reside (e.g. shallow wells $<0.5\ \text{eV}$ are effectively mobile or solute at 300 K and above, while D in deep wells $>1.4\ \text{eV}$ are “trapped” and immobile). By measuring the time-dependence of D concentration and how it reacts to changing conditions this can help us distinguish the trapped (static) D from the solute/mobile (dynamic) D.

3.3. Trap production from irradiating 3.5 MeV ^3He ion beam

Ion beam analysis, such as NRA, is typically considered as a non-perturbing diagnostic and this is usually true for the case of post-mortem analysis where beam fluence is small with large detector solid angles. However, in a dynamic experiment, such as DIONISOS, where NRA is occurring during the plasma discharge, the ion beam is not only a diagnostic, but also a potential cause of damage in the material. A set of exposures was performed to further investigate this effect. For these tests a new Mo specimen was used for each exposure to the ^3He beam and plasma as opposed to the data acquired in Fig. 3 where the Mo targets were re-used after thermal desorptions.

The clearest indication of the influence of the ^3He analyzing beam can be seen in Fig. 5(a), where the final retention in the first 5 μm of the surface is much greater when the ion beam is present during the entire plasma exposure, rather than a “plasma only” exposure. Evidently a fraction of the Mo lattice atom displacements caused by the irradiating high-energy ^3He ions are converted into permanent lattice defect sites (i.e. vacancies, dislocations, voids) where hydrogenic isotopes can be trapped and stored [14–16]. In addition the implanted D from the plasma can adequately diffuse to these sites in order to “fill” traps at this target temperature (see Section 3.2). What remains an open question is how significant the contribution from displacement-produced trap sites is with respect to the overall retention

properties of the Mo. From Fig. 5(a), the total retention in the first 5 μm of the surface for the ^3He -irradiated target is $3.9 \times 10^{22}\ \text{D/m}^2$ and for the un-irradiated target is $0.44 \times 10^{22}\ \text{D/m}^2$. Thus, the displacement-induced trap sites are the dominant trap source in these experiments, contributing $\sim 85\%$ of the total trap sites in the Mo for the conditions in Fig. 5. A conversion rate for dpa to trap concentration can be estimated by taking the difference between the two curves in Fig. 5(a) to isolate the contribution by the ^3He irradiation and then relating this to the dpa profile determined by SRIM [12] (using 30 eV displacement energy for Mo) (Fig. 5(b)). This conversion rate is highest at the surface despite this being a region of relatively low total damage. In fact the D/Mo profile does not have any indication of enhancement near the ^3He end of range perhaps indicating a synergistic effect between the implanted D from plasma exposure and the ^3He irradiation-produced displacements, and certainly a complicated, likely non-linear, relationship between dpas and traps.

This motivates us to examine explicitly the scaling relationship between average dpa and trap concentration. In these experiments, Mo targets (new target used for each exposure) were exposed to identical plasma and surface conditions ($\Gamma_{\text{D}} = 1 \times 10^{21}\ \text{D/m}^2\ \text{s}$, $V_{\text{bias}} = 100\ \text{V}$, $T_{\text{Mo}} = 500\ \text{K}$, $\Phi_{\text{D}} = 1.5 \times 10^{24}\ \text{D/m}^2$) but increasing 3.5 MeV ^3He fluences by varying the ion beam current irradiating the target during the plasma exposure. Fig. 6 shows the trap concentration integrated over the first 5 μm of the surface as a function of 3.5 MeV ^3He fluence. The dependence of trap density on ^3He fluence (and thus dpa level) scales in a less than linear fashion and can be qualitatively fit to a scaling $(\text{dpa})^\alpha$, where $\alpha = 0.25\text{--}0.5$.

3.4. Dynamic retention and D release

The surface release rate of hydrogenic species is of crucial importance in understanding how hydrogenic retention in the walls of long-pulse and steady-state fusion devices will evolve. Although the depth resolution is limited with NRA to $\sim 500\ \text{nm}$, DIONISOS allows us to diagnose the time-dependence of the D concentration in the surface region, with and without the plasma driving permeation. This allows us to examine the relative quantities of D residing in shallow (solute) and deep (trapped) energy sites. Similar techniques of using NRA to determine near-surface solute concentrations have been used with neutral gas experiments [17].

On implantation from the plasma, the deuterium release from a surface, Γ_{out} , can be rate-limited by two processes: diffusion or surface recombination. In the case of diffusion the efflux is limited by the diffusivity, d , and near-surface solute density, $n_{\text{D},0}$, gradient from the implantation depth, δ , back to the surface, i.e. $\Gamma_{\text{out}} < d n_{\text{D},0}/\delta$. In the second case recombination of two atomic D into volatile D_2 at the surface limits the D release, i.e. $\Gamma_{\text{out}} < 0.5 n_{\text{D},0}^2 R$ where $R\ (\text{m}^4/\text{s})$ is the recombination coefficient.

The DIONISOS system has been utilized to determine $n_{\text{D},0}$, thus providing insight into the rate-limiting surface-efflux mechanism. Once the plasma is removed the concentration of near-surface solute D, $n_{\text{D},0}$, will return to the natural solubility levels of the material ($<1\ \text{appm}$ for Mo at this T and ambient gas pressure) and the trapped D, by definition, will remain unchanged. Therefore, the approximate measurement of $n_{\text{D},0}$ is the immediate (within time resolution of NRA) decrease in the total (solute + trapped D) measured density in the top surface slab back to the trapped D concentration only. We denote this measured density decrease $\Delta n_{\text{D,surf}}$. An example of such a measurement is found in Fig. 7(a) where $\Delta n_{\text{D,surf}}$ is clearly determined. The compilation of $\Delta n_{\text{D,surf}}$ for different exposure conditions is shown in Fig. 7(b).

There is a clear decrease in $\Delta n_{\text{D,surf}}$ with increasing target bias. If the release of D from the surface was diffusion-limited one would expect to see $\Delta n_{\text{D,surf}}$ increase with increasing implantation depth (higher D^+ energies), since the diffusivity and incident flux are con-

stant. However the experimental trend is the opposite. An additional characteristic of the data, consistent with recombination as the rate-limiting process for surface loss, is that the $\Delta n_{D,surf}$ values organize well to an Arrhenius relationship. One does not expect a direct dependence of R on incident ion energy. However we believe this is a result of the higher energy D ions inducing more sputter cleaning of the surface; cleaned Mo surfaces in general have increased recombination rates [18,19].

Under the assumption that recombination is the rate-limiting process for surface loss we can infer an effective surface recombination coefficient, R , through the equilibrium condition of $\Gamma_{out} = \Gamma_{in}$; so $\Gamma_{D+,in} = 0.5 \Gamma_{D2,out} = 0.5 (n_{D,0})^2 R = 0.5 (\Delta n_{D,surf})^2 R$. Our inferred R values (Fig. 7(b) right-hand axis) are at the lower end of surface recombination coefficients measured for tungsten [20,21] and much lower than those predicted by theory [22]. Part of this discrepancy can be explained by the non-ideal surface of the Mo targets. Contrary to other recombination studies where the surface is sputter-cleaned and annealed [17–20], our targets underwent no special preparations of the surface (rough, un-annealed, etc.). While this makes it more difficult to compare the R values to theory, it more closely resembles the conditions inside a tokamak where low-Z surface impurities are ubiquitous.

We note that the inferred R values in this study can only be considered an effective surface recombination coefficient in the sense that it is the limiting factor of the release of D from the surface. Since we are limited to a depth resolution of 500 nm, other processes may be included in this R value that are not considered in theory or more carefully factored out in more precise experiments. Regardless of the interpretation, the important insight is that the near-surface solute (mobile) D concentrations are significantly enhanced compared to intrinsic solution expectations, and measuring

this directly gains important insights into the physical processes at play.

4. Discussion

The absence of a peak in the retention at the end of the ^3He ion range, where the ^3He irradiation damage is concentrated is probably related to a number of factors. The non-linear relationship between trap concentration and dpa (Fig. 6) will help to “flatten” the distribution of traps created by ^3He irradiation. At 300 K, we know the implanted D cannot diffuse into the material far enough in a 1500 s exposure to reach the deep ($>3 \mu\text{m}$) trap sites produced by the ^3He irradiation. At 400 K, the leading edge of the deuterium is just reaching the end of the ion range after 1500 s, so the deep trap sites are just beginning to fill (Fig. 4). At the higher temperatures, where the implanted D has greater access to the ^3He irradiation traps, other effects may be activated, such as higher rates of trap annealing or trap diffusion. Certainly the diffusion/mobility of traps would help flatten any peaks in the trap distribution. Also, as vacancies become mobile at higher temperatures, they are more likely to encounter a grain boundary or interstitial atom and repair themselves thereby removing a potential trap site from the lattice.

The peaked retention at the surface could be explained by several effects. Since the Mo targets are un-annealed, it is possible there is a large concentration of inherent traps at the surface due to fabrication and machining stresses. However, if this were the case, one would expect the D concentration in the near-surface to be the same for all exposures, but the data shows the D retention near the surface decreases with increasing temperature (Fig. 3(b)). This could be explained if these inherent trap sites had a low trapping energy. Another possible explanation of peaked retention at the surface is that the plasma implantation is producing trap sites. Studies in tungsten have shown that exposure of materials with low solubility to high plasma fluxes can “super-saturate” the material and produce stresses in the lattice that are relieved through the production of dislocations and vacancies [23–25]. Connecting trap production to plasma flux could also be part of the explanation as to why the retention in the 100 V exposures is the same as the 30 and 350 V exposures despite receiving less ^3He fluence. It is also possible that the simultaneous implantation of D with the He^3 damage may have a synergistic effect; the D could be filling vacancies making it harder for them to recombine with interstitials or annihilate at grain boundaries. This could lead to a significant enhancement of trap production in the near-surface where the implanted D atoms have more immediate access to the traps.

5. Conclusions

The unique capability of DIONISOS to dynamically measure D retention allows for these first experimental measurements of deuterium release rates during and after a plasma exposure. From these release rates an “effective” surface recombination coefficient can be inferred. The inferred values are lower than those predicted by theory and measured for tungsten. This might be expected given the unprepared nature of the Mo surfaces (i.e. dirty, rough, etc.) and the fact that poor depth resolution means other processes may be included in these values rather than a pure measurement of surface recombination. However, the release rate from impure, unprepared surfaces will be critical to understanding fuel retention in the walls of ITER and other long-pulse or steady-state fusion devices.

The unique conditions produced in the DIONISOS experiment have also yielded important insights into the behaviour of hydrogenic retention in Mo in a nuclear environment. Irradiation with MeV-energy particles leads to significant enhancement of trap

Fig. 7. (a) The D depth profile immediately before and after the plasma is turned off demonstrating how $\Delta n_{D,surf}$ is determined, and (b) The $\Delta n_{D,surf}$ values for all exposures in Fig. 3 and the corresponding inferred surface recombination coefficient (R).

densities spread throughout the measurement range. At elevated temperatures, $T_{\text{Mo}} > 500$ K, implanted D from the plasma can access these traps, which results in significant retention distributed throughout the entire ^3He ion range. At this time we cannot with certainty determine the absolute contributions of the various effects of solute D diffusivity, trap migration, and trap annealing/annihilation. It is our interpretation that the conditions for highest retention appear to be a Mo target of intermediate temperature (400–500 K) exposed to a high fluence of MeV irradiating ions as this maximizes retention by allowing the implanted D to populate the MeV ion-produced trap sites. Certainly one would expect at the higher temperatures (700 K) thermal de-trapping and trap annealing can begin to play a role and overall retention can begin to decrease. Operation at much higher temperatures (>700 K) would appear to help alleviate hydrogenic retention concerns even in a neutron environment. Clearly more research on retention behaviour in a nuclear environment is needed as the presence of MeV ions (or neutrons) appears to be a dominant factor for retention in high-Z materials.

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Appendix 3

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On the consequences of neutron induced damage for volumetric fuel retention in plasma facing materials

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ABSTRACT

In burning deuterium–tritium (D–T) fusion experiments, such as ITER, plasma-facing components (PFCs) will for the first time be subject to intense 14 MeV neutron bombardment, which cause displacement damage uniformly distributed throughout PFCs. A literature review indicates these displacements typically lead to hydrogenic trap sites $\sim 1\%$ solid concentration in refractory metals tungsten (W) and molybdenum, a level reached within ~ 1000 ITER shots. Simple analytic and numerical models indicate this is a concern for reaching the T fuel retention limit in ITER of 350 g, mostly due to the efficient permeation of D/T into the W allowing access to the volumetric trap sites. The sensitivity of the retention results to the incident plasma parameters, PFC temperature, surface flux balance model and plasma duty-cycle is explored. Within the range of experimental and model uncertainties a limit for an all-W ITER divertor is found ~ 100 – 1000 s of shots. It is shown that ambient temperatures in excess of ~ 1000 K could control T inventory in a W-clad reactor despite the presence of large trap concentrations, an option which is not possible for ITER with water-cooled walls.

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1. Introduction and motivation

The control of bred tritium (T) fuel will be critical for the operation of large-scale burning plasma experiments (e.g. ITER) and future magnetic fusion reactors. A particular concern is in-vessel retention of T, arising both from safety limits of “unaccounted” T, and in reactors, the requirement to recover unburned tritium from the vessel so as to not impact the global fuel cycle. These limits are both important; the former to the public perception of fusion as a safe energy source, and the latter to the scientific viability of operating a steady-state fusion device. ITER, as an example D–T burning plasma, has a regulatory in-vessel tritium inventory limit ~ 0.3 kg [1]. For an eventual reactor the cycling inventory of T will be ~ 10 s kg, and given that blanket T breeding ratios (TBR) are barely above unity (typical TBR ~ 1.05), an in-vessel accumulation ~ 10 kg/(TBR–1) ~ 0.5 kg will deleteriously impact the fuel cycle. Therefore a conservative approach is to aim to <0.3 kg of T retention to not impact ITER or reactor operation.

The success of a burning plasma is defined by its ability to generate 14 MeV neutrons from thermonuclear D–T reactions in the plasma core. The plasma-facing components (PFCs) necessarily reside in this neutron (n) flux. The neutrons have long collision distances (typically >0.1 m) in solid materials. Therefore n-induced atomic displacements in the PFC (and other effects such as helium production) will be produced volumetrically, i.e. evenly distributed through the PFC thickness ~ 1 – 2 cm. It seems likely that these

displacements could produce volumetric hydrogenic (H) traps, i.e. potential wells in the material in which H can reside out of solution.

Simultaneous with n bombardment, PFC materials are under intense H ion and atom bombardment on their plasma-facing sides. If a PFC material allows permeation of the H from the surface through its volume, this evidently raises concerns that the permeating H fuel will “find” the volumetric traps and increase fuel retention (see [2] for a review of this topic). The volume of PFCs present an enormous possible H sink; for example 1% volumetric fraction of D/T in 1 cm thick, 1000 m² PFC would represent ~ 10 kg of tritium retention. The purpose of this article is to explore the issues arising from this concern. We use the refractory metal tungsten (W) as an example PFC of concern due to its high permeation of H, and its projected use in the ITER experiment [1] and future fusion devices (e.g. ARIES-AT [3]). ITER is used as a prototypical large-scale burning plasma experiment, although the exploration is meant to be general to the use of H-permeable PFCs in a neutron environment.

2. Basic estimates

2.1. Displacement-induced volumetric traps

We wish to relate neutron-induced displacements to trap density, n_{tr} (m^{−3}). Unfortunately, no large-scale 14 MeV neutron source is available, so one must rely on experiments that bombard refractory metals, W and molybdenum (Mo) with high-energy (>1 MeV) ions. Such experiments “simulate” volumetric n-induced

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displacements since their range (>micron) is much larger than plasma ion implantation depths (~nm).

Measured H trap density induced by high-energy ion bombardment of refractory metals is summarized from literature sources in Fig. 1, organized by displacements per atom (dpa). Oliver et al. [4] used 800 MeV protons (p) on W to produce 0.3 and 7 dpa. The high energy of the protons leads to volumetric damage (p ion range in W ~ 0.2 m), of which ~60% is caused by spallation neutrons. Thermal desorption spectroscopy (TDS) and modeling inferred a trap/solid fraction $f_{tr} \sim 7\%$ for both dpa levels ($f_{tr} = n_{tr}/n_{solid}$, $n_{solid} = n_{W}/M_o \sim 6.5 \times 10^{28} \text{ m}^{-3}$ is used throughout). Takagi et al. [5] and Wright et al. [6,7] exposed Mo to ^3He ion beams of 0.8 and 3.5 MeV energies, respectively, plus D plasma exposure, and found $f_{tr} \sim 1\%$ as measured by Nuclear Reaction Analysis (NRA). Note f_{tr} is averaged D/Mo from NRA through the ^3He implantation range (~1–5 μm), and therefore assumes 1 D/H per trap, a convention we adopt throughout for simplicity. Plotted dpa are calculated vacancies per ion (SRIM [8]) as averaged through the ion range, which seems justified given that traps were not particularly located at the end-of-range.

Overall, the trap concentration tends to plateau at $f_{tr} \sim 1\%$ and not increase strongly for >0.3–1 dpa. The reason for this may be related to an equilibrium between displacements both creating and healing traps. The “plateau” $f_{tr} \sim 1\%$ greatly exceeds typical “intrinsic” $f_{tr} \sim 10^{-5}$ for annealed refractory metals [9]. While 800 MeV p-induced spallation neutrons provide the best simulation of truly volumetric damage, TDS is difficult to interpret since the trapped H density, along with other important parameters/assumptions such as trap activation energy, must be obtained from a fit to the thermal desorption spectrum versus temperature [4]. While NRA has the advantage of directly measuring n_{tr} , it can only be obtained up to the depth of the ion range (<10 μm); TDS diagnoses trap density throughout the bulk of the material, which is of the most interest to our study. Therefore we adopt the policy of relying on NRA for the best absolute measure of n_{tr} , but rely on TDS for the trends.

Fig. 1. Database of hydrogenic trap evolution versus displacements per atom. Literature source, irradiation conditions (beam species, energy), exposure temperature and trap diagnosis method are listed in the legend. Equivalent 500 MW ITER discharges are also shown.

For this study we adopt the solid line in Fig. 1 as the trap production rate vs. dpa, which uses Oliver et al. data to interpolate a linear increase of traps/dpa ~ 0.2 starting with un-irradiated samples ($f_{tr} = 0$), arriving at a constant $f_{tr} = 1\%$ for >0.05 dpa as measured by NRA (this sets $f_{tr} \sim 0.7\%$ at 1000 ITER shots). Obviously several other interpretations of Fig. 1 are possible and more data would be desirable, but this seems a reasonable starting point for the study. Note that at the low exposure temperatures in Fig. 1 the traps will not thermally anneal.

2.2. Simplistic permeation of H

Given that neutrons produce volumetric traps, permeation of the H to these empty traps, driven by large H flux densities at the PFC surface, should control retention rates. The standard diffusivity of H in W is taken from [10] as $D(\text{m}^2\text{s}^{-1}) = 4.1 \times 10^{-7} \exp(-E_D/kT_{PFC})$ where $E_D = 0.39 \text{ eV}$, k is the Boltzmann constant and $T_{PFC}(\text{K})$ is the material temperature. A simplistic analytic model [11] of H permeation in W at constant temperature can estimate if the retention rate is of concern. The H permeation “front” will be at a depth $s = (2Dt)^{1/2}$ at time $t(\text{s})$ of the exposure. The effective flux density of traps uncovered by the moving front will be $\Gamma_T (\text{H-m}^2 \text{s}^{-1}) = n_{tr} v_{front} = n_{tr} ds/dt = n_{tr} (D/2t)^{1/2}$, which act as a sink to the permeating H. The “source” of H can be estimated by assuming a linear H solute density n_H from the front surface where $n_H \equiv n_{H,0} = \text{constant}$, to $n_H \sim 0$ at s . Therefore the source $\Gamma_H (\text{H-m}^2 \text{s}^{-1}) = D \nabla n_H = D n_{H,0}/s = n_{H,0}(D/2t)^{1/2}$. Examination of Γ_T and Γ_H informs us that if $n_{H,0} \sim n_{tr}$ then the rate of retention is *not* limited by the solute H source, and also indicates that $n_{H,0}$ is a critical boundary condition.

In Fig. 2 we show the permeation front, s , and the cumulative retention of $T(\text{g-T}) = (m_T/2) A_{PFC} \int \Gamma_T dt$, for the case of the ITER divertor (W only PFC, area $A_{PFC} \sim 210 \text{ m}^2$, triton mass $m_T \sim 5 \times 10^{-24} \text{ g}$, PFC thickness = 2 cm) assuming $n_{H,0} = n_{tr}$ and a 1:1 D:T mix. The trap density is time-dependent as described in Section 2.1, and n_{tr} is considered permanently trapped. Fig. 2 shows that the H is highly permeable in W, reaching 1–10 mm on the time-scale equivalent of 100s ITER shots (400 s/shot). As a result the T limit ~350 g can be reached in ~200–600 shots, indicating this issue could be a concern if $n_{H,0} \sim n_{tr} \sim 10^{-3} - 10^{-2} n_W$. Note that here the retention rate is *faster* at higher temperature, solely due to the

Fig. 2. ITER divertor analytic model with $n_{H,0} = n_{tr}$. Trap/dpa = 0.2. (Lower panel) Permeation distance into W. (Upper panel) Cumulative total T retention with no de-trapping.

higher H diffusivity. This simply points out that the benefits of high T_{PFC} (examined below) in reducing retention must be balanced against the enhanced permeation of H to the traps.

3. Scoping T retention in ITER with a numerical model

Beyond the simple analytic model above, one must use a numerical model to scope the sensitivity of the expected T retention to $n_{\text{H},0}$, T_{PFC} , exposure history, etc. The purpose of the model is to have a simplified material model (compared to say TMAP [12]) but with highly flexible time and spatial dependencies and rapid execution. The 1-D slab model solves the coupled continuity equations for solute H, n_{H} , and trapped H, n_{T} , namely:

$$\frac{\partial n_{\text{H}}}{\partial t} + D \nabla_s^2 n_{\text{H}} = -R_{\text{trap}} n_{\text{H}} + R_{\text{de-trap}} n_{\text{T}} \quad (1)$$

$$\frac{\partial n_{\text{T}}}{\partial t} = +R_{\text{trap}} n_{\text{H}} - R_{\text{de-trap}} n_{\text{T}} \quad (2)$$

Traps, and therefore trapped H, are taken to be immobile (uniform in s). The form of trapping and de-trapping rate are taken from [12] as

$$R_{\text{trap}} = \frac{D n_{\text{tr}}}{\lambda^2 n_{\text{W}}} \quad R_{\text{de-trap}} = \nu \exp\left(\frac{-E_{\text{tr}}}{kT_{\text{PFC}}}\right) \quad (3)$$

where λ is the distance between empty traps, $\nu \sim 10^{13} \text{ s}^{-1}$ is the bounce frequency of H in traps and $E_{\text{tr}} \sim 1.5 \text{ eV}$ is the trap activation energy, typical of E_{tr} found in the studies of Section 2.1. The W PFC thickness is 2 cm. A zero-gradient n_{H} is imposed on the back of the deepest slab, which is equivalent to placing a permeation barrier between the W PFC and heat sink.

The numerical model is used to study the effect of changing the ratio $n_{\text{H},0}/n_{\text{tr}}$ in Fig. 3 for a simple case of constant f_{tr} and no de-trapping ($R_{\text{de-trap}} = 0$). The analytic model of Section 2.2 (dashed line in Fig. 3) is close to the $n_{\text{H},0}/n_{\text{tr}} = 1$ case, as expected. If $n_{\text{H},0}/n_{\text{tr}} > 1$ then the exponential-like leading trail ahead of s_{front} (from actually solving the diffusion equation) allows the deep traps to fill even faster, with all the traps being filled eventually. Conversely if $n_{\text{H},0}/n_{\text{tr}} < 1$ the retention continues to increase with time (again due to the finite H source caused by the leading trail) but at a decreased rate.

We use two models to establish a reasonable bound on $n_{\text{H},0}/n_{\text{tr}}$. In general we expect $n_{\text{H},0}$ to be set by the dominant rate-limiting process for release of H from the surface, which is roughly equal to the incoming H flux of ions/atoms, $\Gamma_{\text{H},\text{in}}$ from plasma contact (small retention rates normalized to incident flux density are as-

sumed here). The “implantation” model assumes that diffusion of the implanted H back to the surface through the distance s_{implant} is the rate-limiting process, so that in equilibrium $n_{\text{H},0} = \Gamma_{\text{H},\text{in}} s_{\text{implant}}/D$, assuming $n_{\text{H}} = 0$ at $s = 0$. This model tends to produce the minimum possible $n_{\text{H},0}$; D_{H} in W is large and shallow implantation depths (~ 1 – 10 nm) are expected in the divertor and surface recombination is not required. The “recombination” model assumes the rate limiting process is recombination of H into volatile H_2 at the surface, so that in equilibrium $n_{\text{H},0} = (2\Gamma_{\text{H},\text{in}}/R)^{1/2}$. The recombination rate coefficient R ($\text{m}^4 \text{ s}^{-1}$) $= 5 \times 10^{-30} \exp(-0.19[\text{eV}]/kT)$ is taken from DIONISOS for 30 eV D^+ exposure [6]. It is important to note that this R was *inferred* based on direct DIONISOS measurements of $n_{\text{H},0}$ during plasma exposure, which found $n_{\text{H},0}/n_{\text{Mo}} \sim 0.1$ – 1% for $\Gamma_{\text{in}} \sim 2 \times 10^{21} \text{ m}^{-2} \text{ s}^{-1}$. While arising from a direct measurement of $n_{\text{H},0}$, the DIONISOS R trends towards lower value of R from other literature sources [9], thus we consider this an *upper* bound on $n_{\text{H},0}$. Note the two models have different power dependencies on Γ_{in} and different T_{PFC} trends due to different activation energies. For ITER simulations we use the values for Γ_{in} and surface T_{surf} as listed in Table 1, which distribute the total divertor flux $\sim 10^{25} \text{ s}^{-1}$ [13] and divertor power ($\sim 50 \text{ MW}$) into three discrete zones. This is meant to be indicative of expected exposure conditions in a large-scale burning plasma, rather than strictly predictive of ITER.

We have scoped the effect of changing exposure parameters, such as imposing a realistic T gradient across the PFC from the front surface to the heat sink ($T = 428 \text{ K}$ in all cases) and the effect of evolving versus constant f_{tr} . Due to limited space, we highlight an interesting sensitivity of the retention to plasma duty cycle in Fig. 4. For simplicity, retention calculations often assume the plasma exposure and T_{PFC} are constant, however in reality ITER will be a pulsed device with a nominal duty cycle of 20%. One may hope that the periodic removal of Γ_{in} , which drives the permeation through $n_{\text{H},0}$, would impede the access of H to the traps. However, Fig. 4 indicates that the retention (per shot) can be *increased* in many cases. This is due to two effects. First the removal of the plasma flux also removes the power flux and the PFC returns to low $T = 428 \text{ K}$, which slows diffusion and precludes significant de-trapping. This tends to “freeze” the H profile. Secondly, since D_{H} is finite between shots, the n_{H} gradient tends to relax both towards the surface *and* deeper into the bulk. However the “emptied” n_{H} profile near the surface is nearly instantaneously refilled when the plasma flux returns, continuing to drive permeation. The result is a ratcheting effect for solute and trapped H deeper in the surface. This result highlights the importance of *ambient* (i.e. heat sink) PFC temperature, although the relative sensitivity to cycling changes from one exposure condition to the next.

Sample results for a W divertor in ITER are shown in Fig. 5. This highlights the general result of the scoping study that the retention is most sensitive to the surface model. Shown is the “realistic” exposure model: linear temperature gradients through the PFC, 20% duty cycle and evolving trap density. This can be compared in Fig. 5 to the limit reached using the usual “simple” exposure: constant $T(s) = T_{\text{surf}}$, 100% duty cycle and fixed trap fraction of 1%.

Fig. 3. Effect of changing ratio $n_{\text{H},0}/n_{\text{tr}}$ in cumulative tritium retention from numerical model. Case shown: $T = 500 \text{ K}$, constant $f_{\text{trap}} = 10^{-3}$, $R_{\text{de-trap}} = 0$.

Table 1

Description of plasma flux, incident particle energy and surface temperature for three ITER W-divertor “zones” used in numerical simulations. Total particle flux to divertor (area = 210 m^2) is 10^{25} ion/s (strikepoint + baffle) and 10^{25} atoms/s (baffle) and total power to divertor delivered by particles is 54 MW. Two centimeter thick W PFC, thermal conductivity $\sim 180 \text{ W/m/K}$ is used.

Region	Area (m^2)	Γ_i ($\text{m}^{-2} \text{ s}^{-1}$)	E_{incident} (eV)	q (MW m^{-2})	T_{surf} (K)
Strikepoint	8	6×10^{23}	30	2.9	~ 760
Baffle	112	4.8×10^{22}	30	0.23	~ 460
Dome	90	5.6×10^{22}	5	0.04	~ 440

Fig. 4. Effect of 20% duty cycle plasma exposure. Case shown: $f_{\text{trap}} = 7 \times 10^{-3}$, “baffle” region of Table 1. (a) Cumulative retained T areal density between 100% and 20% duty cycle versus plasma shot number (b)–(d) 20% duty cycle. (b) Trapped H density, n_T , at different depths s , (c) surface temperature showing thermal pulsing, (d) solute H density, n_H , at different depths. For different s values the amplitudes of n_T and n_H have been arbitrarily scaled for viewing clarity.

In fact the exposure model has opposite effects with the two surface models: increasing the limit to ~ 200 shots from ~ 20 shots for the recombination model and decreasing the limit to ~ 1000 shots from ~ 2500 shots for the implantation model. We note this last result is in good agreement with DIFFUSE calculations [14] which indicate a limit ~ 2500 shots using a similar surface and exposure model (benchmark cases for specific exposure conditions of our model are also within $< \text{factor of } 2$ of DIFFUSE results). The model is therefore deemed numerically accurate, however this exercise indicates that the expected results for retention shot limits in ITER are sensitive to assumptions in the modeling.

4. Discussion and conclusions

The results of Fig. 5 indicate ITER scenarios where the T limit may be met in 100s–1000s of shots due to T retention in a W divertor. It is important not to view these as “predictions”, since no present model (including our simple one) can capture the true complexity of the evolutions of PFC surface and materials in ITER (for example it will not be true that all plasmas will be the same Table 1, low-Z impurities will likely be present in the divertor, disruptions are ignored, etc.). *Rather this serves as a gross indication that volumetric trap production is a concern with refractory metal PFCs due to a simple picture of permeation to volumetric traps.* For

Fig. 5. Summary of T retention results for ITER. Lines show “Full” exposure model: T gradient through PFC, 20% duty cycle, evolving f_{tr} as in Fig. 1. (a) Recombination surface model (b) Implantation surface model. Stars indicate shot where limit $T = 350$ g is reached with “simple” exposure model described in text, but the same surface model.

ITER this serves to indicate that one may likely require recovery of tritium from the bulk of W PFCs during its operational lifetime, which is not addressed in the present operational scenario (for example maximum divertor bake $T \sim 240$ C [1] is inadequate for T desorption from the bulk). Looking past ITER to a steady-state device the optimistic limit estimates presented here of ~ 2500 shots are the equivalent of only ~ 10 days exposure, obviously a concern if operation for ~ 1 year are expected.

A simple model indicates that the key to controlling T retention in W with n-induced traps is, not surprisingly, ambient temperature. If one considers a steady-state reactor/DEMO we can reasonably expect that (a) the PFC/blanket temperature will be required to be high (> 900 K) for thermal–electric conversion efficiency (e.g. ARIES [3]) and (b) therefore the H will be fully permeated through the PFC depth. An unknown is the equilibrium n_{tr} that would be achieved by combining continuous n damage plus annealing from relatively high T_{PFC} (compared to T_{PFC} of data in Fig. 1). Rather we consider the pessimistic assumption that f_{tr} will remain $\sim 1\%$, but that de-trapping will be sufficiently strong to leave the traps empty. Taking a steady state solution ($\partial/\partial t \rightarrow 0$), Eq. (3) can be rewritten to solve for f , the fraction of traps that are filled, as:

$$\begin{aligned} \frac{f}{(1-f)^{2/3}} &= \frac{D n_{\text{tr}}^{2/3} n_{\text{H},0}}{n_{\text{W}} v_{\text{bounce}} \exp(-E_{\text{trap}}/kT)} \\ &= \frac{n_{\text{tr}}^{2/3} \Gamma s_{\text{implant}}}{n_{\text{W}} v_{\text{bounce}} \exp(-E_{\text{trap}}/kT)} \end{aligned} \quad (4)$$

Fig. 6. Total T retention for ITER as if operating steady-state with varying ambient constant PFC temperature. Case: $f_{tr} = 1\%$, implantation model (Eq. (4)).

where the spacing between empty trap sites is estimated as $\lambda \sim (n_{tr} - n_T)^{-1/3} = n_{tr}^{-1/3}(1-f)^{-1/3}$. In the last term of Eq. (4) we substitute the implantation model for $n_{H,0}$ which removes the dependence on D . Taking $f_{tr} \sim 1\%$ and the ITER exposure/ T_{PFC} model (Table 1) plus a low flux-density W main wall (area $\sim 600 \text{ m}^2$, $\Gamma_{in} \sim 10^{21} \text{ m}^{-2}\text{s}^{-1}$) produces the results shown in Fig. 6. This calculation indicates that ambient $T > 1000 \text{ K}$ are required to reduce the retained T to acceptable levels, but this can be achieved even in the presence of large $f_{tr} \sim 1\%$. Again this should be taken as indicative (rather than predictive) that for a fixed exposure condition there will exist a sharp minimum ambient T_{PFC} for operating the W PFCs in order to assure acceptable T retention levels.

The preceding exercise also illustrates the difficulty in vetting PFC T retention in ITER or any pulsed, water-cooled device where maximum ambient $T < 500 \text{ K}$. In such devices, the PFC is heated only simultaneously with plasma flux, while intra-shot periods freeze the solute and trapped H deep in the PFC. This is the worst-case scenario for driving permeation in the presence of

volumetric traps caused by neutrons in a successful burning plasma experiment. Therefore, one cannot expect the T retention of W in ITER to be indicative of what will occur in a reactor. This observation also affects the rationale for using W in ITER; one should not necessarily expect W to readily “solve” tritium retention, but rather one is motivated to test other aspects of W such as its erosion resistance, the effect of W on the burning plasma performance and neutron-damage resistance.

Beyond the obviously strong influence of temperature, the present study clearly motivates more experiments and modeling towards better understanding trap production/healing mechanisms in different radiating environments, deep permeation of H in W, and the complex coupling of the two.

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Appendix 4

THE DYNAMICS OF HYDROGENIC RETENTION IN IRRADIATED MOLYBDENUM

by

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A dissertation submitted in partial fulfillment of
the requirements for the degree of

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ABSTRACT

A new experiment on the Dynamics of ION Implantation and Sputtering Of Surfaces (DION-ISOS) was designed, commissioned, and assembled for this thesis to investigate the dynamics of hydrogenic retention in irradiated molybdenum (Mo). The thesis is motivated by the need to better understand the retention of hydrogenic fusion fuel, including radioactive tritium, in plasma-facing refractory metals in present and future magnetic fusion devices. This experiment exposes surfaces to high flux density ($\sim 10^{21}$ D/m²s) deuterium plasmas to a fluence of $\sim 1.5 \times 10^{24}$ D/m², while simultaneously monitoring the deuterium (D) concentration as a function of depth over the first 5 μm with nuclear reaction analysis using 3.5 MeV ^3He ions. These experimental capabilities allow for the evolution and dependencies of retained D, which resides in energy traps in the Mo, to be directly measured under fusion-relevant conditions.

Experimental results are taken over a range of Mo temperatures (300-700 K) and plasma ion energies (30, 100, and 350 eV; typical of the range for D ions in fusion experiments) for 99.97% pure Mo plate. Hydrogenic retention in the first 5 μm of the surface is found to have very weak dependence on plasma ion energy. The highest retention in the first 5 μm ($\sim 2.5 \times 10^{21}$ D/m²) was found at 400 K where the retention scales linearly with the incident D fluence and the lowest retention ($\sim 7.5 \times 10^{20}$ D/m²) was at 300 K where the D is diffusion limited to the first micron of the surface. The 3.5 MeV ^3He diagnostic beam irradiates the surface, creating displacements in the Mo, concentrated at the end of the ion range of $\sim 5 \mu\text{m}$. The relationship between these beam-induced displacements, which serve as a proxy for neutron-induced damage in a fusion reactor, and resulting D trap density have been quantified as a function of displacements per atom (dpa) with a

non-linear relationship of traps/atom = $0.00015(\text{dpa})^{1/4}$ found. With available trap sites in the bulk of the material, the diffusion of the solute D to the trap locations becomes the limiting process for retention, explaining why the retention was the lowest at 300 K where D diffusion is weak in Mo. Measurements of the dynamic D inventory in the surface layer allow the surface recombination rate, which sets the limit for D recombining into D_2 in order to be released from the Mo surface, to be calculated for all ion energies and surface temperatures. The surface recombination rate is found to increase with surface temperature, as expected, and with increasing ion energy, likely due to the sputtering of thin surface impurity/oxide layers.

Modeling of the experimental results with a 1-D, numerical, flux-conservation slab model, yields a solute D diffusion rate of $D_{Do}=4 \times 10^{-6} \exp(-0.63 \text{ eV}/kT_{mo})$. Modeling also shows that traps and trapped D are mobile at elevated temperatures and are able to diffuse deep into the bulk, well past the detection range of the nuclear reaction analysis. This indicates that the hydrogenic retention seen in the first $5 \mu\text{m}$ of the surface for $T_{mo} \geq 500 \text{ K}$, is a fraction of the total retention in the Mo bulk. Experimental results and modeling also indicate a plasma-induced trap production mechanism that scales linearly with plasma flux density. It is hypothesized that this is a pressure-driven trap production mechanism caused by the high flux density of implanted ions in combination with the low hydrogenic solubility of Mo. A tungsten lamellae target at 400 K is exposed to a 30 eV/D+ plasma to compare the retention of these high-Z materials. The tungsten lamellae is found to have hydrogenic retention rates a factor of 6-7 lower than Mo. This is mostly due to the much lower diffusion rate of D in tungsten at this temperature, which inhibits the D from diffusing to trap sites.

A Mo tile, previously exposed in the Alcator C-Mod tokamak, has a boron-rich ($\sim 12 \text{ at\%}$), $0.5 \mu\text{m}$ thick layer on the surface and shows lower retention rates than the pure Mo plate in the first $5 \mu\text{m}$ of the surface. This is due to reduced D and trap diffusion in the boron-rich layer that limits the access of the implanted D to the irradiation traps in the bulk of the tile. The C-Mod tile characteristics and hydrogenic retention properties of Mo found in DIONISOS are entered into the numerical model used to simulate a 3 s plasma discharge in the Alcator C-Mod divertor, including the temperature rise and cooling caused by the plasma exposure and inertial cooling. The

results of the simulation show that 0.35% of incident ions are retained in the Mo. The retention is linear with time and shows no signs of saturation after repeated simulated exposures. This agrees with experimental results from Alcator C-Mod operating with "clean" Mo walls that indicate high D retention rates with a Mo wall. The simulation indicates that the retention is caused by the simultaneous high particle flux and heating from a plasma exposure, followed by rapid cool-down after the plasma discharge that effectively "freezes" the D in the Mo bulk.

The combination of MeV-particle irradiation of a surface, high incident plasma flux density, and sustained high temperatures can lead to high levels of hydrogenic trapping deep into the bulk of Mo. Unfortunately, these are the exact conditions for the ITER divertor region, implying high-Z metals, specifically tungsten, may have unfavorable hydrogenic retention characteristics in the ITER divertor and future fusion devices.

Chapter 1

Introduction

1.1 Review of Plasma-Facing Components

In magnetically confined fusion reactors, closed magnetic field lines contain the hot, energetic core plasma, but confinement is limited to the closed field lines. Outside the last closed flux surface, magnetic field lines directly intercept material surfaces, making contact with a solid surface unavoidable. Plasma-facing components (PFC) are, by definition, the first material in contact with the plasma contained in a fusion reactor. The PFC must endure a combination of high heat loads (both steady-state and transient), high fluxes of low energy plasma ions, charge-exchange (CX) neutrals, and, during DT-burn operation, and bombardment by 14 MeV neutrons. To withstand these conditions and have minimal impact on plasma operations an ideal PFC would have: high thermal conductivity and thermal stress resistance, low or no erosion, minimal hydrogenic fuel retention, and resilience against neutron irradiation and activation. It would also be beneficial if the PFC material was inexpensive, readily available, and easily machinable.

ITER is an international research project to construct the first D-T burning plasma with an energy amplification factor of $Q=10$ and sustained fusion power ~ 500 MW for up to 400 seconds. Because its performance parameters are prototypical of a magnetic fusion reactor, ITER poses many challenges to PFC design and boundary plasma physics. In the ITER design, steady-state heat loads are expected to reach $5\text{-}10\text{ MW/m}^2$ at the strikepoints in the divertor with slow transients (~ 10 s) of heat loads of up to 20 MW/m^2 [1, 2]. At other locations in the divertor (dome, baffles, etc.) the heat load is expected to be $\sim 1\text{-}5\text{ MW/m}^2$ and outside the divertor (main wall) heat loads can range up to $\sim 1\text{ MW/m}^2$ [1, 2]. In the divertor region, the thermo-mechanical requirements for

a PFC are so severe that it eliminates almost all materials except for those with the highest combination of heat conduction and melting temperature. The only materials currently used for divertor construction are tungsten (W), molybdenum (Mo), or carbon (C) and carbon-based materials such as carbon-fiber composites (CFC). At the main wall, where the heat loads are less strenuous, there are more PFC options, however other limitations (sputtering yields/component lifetimes, hydrogenic retention, radiation properties) can also eliminate most of these options. Molybdenum, the focus of this study, is only used on present devices and due to activation issues cannot be used in ITER. However molybdenum serves a close proxy to tungsten in present devices which have lower core plasma temperatures, i.e. the ratio of ionization energies to plasma temperature is about the same for Mo in Alcator C-Mod (a Mo-clad tokamak) as W in ITER.

Besides high heat loads, PFC are also exposed to high flux densities, $10^{20} - 10^{24} m^{-2} s^{-1}$, of low energy plasma ions and lower fluxes, $10^{18} - 10^{19} m^{-2} s^{-1}$, of 50-500 eV CX neutrals [3]. Particle bombardment of a surface can sputter PFC impurity atoms back into the plasma. The physical sputtering yields depend on the mass ratio of the incident particle and the PFC atom, the PFC surface binding energy, and the incident particle energy. A higher mass PFC material will have a lower sputtering yield than a low-Z PFC material for H plasmas, due to the larger mass difference with respect to the plasma H ions. Therefore, the higher mass (high-Z) PFC materials contribute fewer impurities to the plasma. However, high-Z plasma impurities are much more perturbing to plasma conditions since radiative losses and fuel dilution effects increase strongly with atomic number. From this it may appear that a higher sputtering yield would be acceptable if the PFC was a “sacrificial layer” of low-Z material, but the overall lifetime of a PFC in a steady-state or long pulse reactor must also be taken into account. The replacement of PFC tiles on a fusion experiment is a costly procedure, in both funds and time, so there is a strong need to maximize the lifetime of PFC, or at least match the blanket lifetime.

The majority of particles that are incident on the PFC in a fusion reactor are hydrogen isotopes, deuterium (D) or tritium (T), in ionic or atomic form. Therefore, it is important to understand how the plasma fuel, D and T, interact with the PFC. When a PFC is exposed to a hydrogenic plasma there is a flux of ions or atoms that are implanted and trapped in the PFC and a flux

of molecules and neutral atoms that are released, sputtered, or recycled, back into the plasma. Both intrinsic properties of the material (e.g. diffusion, solubility, surface recombination rate) and plasma exposure conditions (e.g. surface temperature, incident flux density, incident ion energy) dictate the rate at which D/T is trapped in the PFC, the total amount of D/T that can be retained in the wall, and the rate of plasma fuelling from the wall. Fuel recycling from the wall must be closely monitored and well understood since it can affect plasma stability by seeding density-limit instabilities and plasma cooling. High net hydrogenic retention in the wall is a concern since it will force higher external plasma fuelling rates to maintain plasma density. There is also a safety risk involved if the hydrogenic retention is too high. Tritium is radioactive (12.3 year half-life, 9800 Ci/g), and the ITER design is only allowed a total in-vessel T inventory of 350 g. This translates to a $\sim 1\%$ T atomic concentration uniformly distributed across the 1000 m² ITER wall to a depth of 0.1 mm, or a 10% T atomic concentration to a depth of 10 microns. Over a 1000 s discharge in an ITER-like device, 100 g of T is fuelled per discharge and $\sim 10\,000$ g of T are passed through the wall surfaces due to the strong plasma recycling. Clearly, the PFC material must have low hydrogenic retention properties to be an effective and safe wall in future fusion devices. Hydrogenic retention is one of the biggest concerns for PFC of next-step fusion devices such as ITER and is an area that, due to its complex nature and difficulty to diagnose, is not well understood in present fusion experiments.

1.2 Hydrogenic Retention Properties of Materials

Hydrogenic retention is not a static problem. It is a dynamic process that occurs throughout a plasma discharge, and can continue after the discharge has ended. We define equilibrium retention as the retention once temperature and H content is constant after a plasma discharge has ended. Dynamic retention is defined as the retention during and immediately after a discharge has ended. Generally, equilibrium retention has a greater impact on tritium inventories, while dynamic retention impacts fuel recycling, although this will depend on equilibrium timescales.

The determining factors for equilibrium retention are the amount of hydrogen that can be retained in a unit volume of the material and what volume was accessible to the implanted ions

during the discharge. The plasma will implant ions into the PFC due to the presence of the sheath boundary. Once implanted, these atoms can diffuse through the material. Hydrogen diffuses in its atomistic form. However, in order for the hydrogen to be released from a surface, it must recombine with another hydrogen to form an H_2 molecule, this is referred to as surface recombination. Because release from the surface requires two hydrogen atoms, the rate of surface recombination is dependent on the square of the hydrogen densities and is a non-linear process. A hydrogen atom may fall into a trap (i.e. an energy well such as a vacancy site, grain boundary, void, bubble, etc) or become solute in the material before reaching a surface and recombining. The retention is comprised of the hydrogen solubility and the trap density of the material. The accessible depth during a plasma exposure is determined by the diffusion rate of the implanted ions and the time scale of the plasma exposure (i.e. $L_{diff} \sim \sqrt{D\tau}$).

Hydrogen solubility is the fractional amount of hydrogen atoms that can be held in the interstitial space of a material. This hydrogen resides in the material but does not occupy a lattice point. Interstitial hydrogen is free to diffuse throughout the material by jumping from one interstitial location to another. The hydrogen solubility of a material is determined by the ambient pressure of hydrogen gas, and the temperature of the material. Solubility, $S \left[\frac{mol}{m^3 \sqrt{MPa}} \right]$, is defined by equation 1.1.

$$S = S_o p^{1/2} \exp \left(\frac{E_s}{k_B T} \right) \quad (1.1)$$

S_o is the solubility coefficient, a material constant, k_B is the Boltzmann constant, p is the ambient pressure of gas, and E_s is the heat of solution, which can be positive or negative depending on whether hydrogen adsorption is endothermic or exothermic. It is found that H isotope dependence on solubility is negligible when compared to other uncertainties in other trapping parameters [4]. For equilibrium retention in fusion experiments, the temperature will be approximately room temperature (RT) or the PFC coolant temperature and the ambient pressure will be very low ($<10^{-4}$ Pa) since all fusion vessels are under high vacuum. For dynamic retention, the PFC can be heated by the plasma and the ambient pressure is also elevated during a discharge from plasma ion recycling and neutral gas injection, and these factors can be important for materials with high H solubility.

Ion implantation from the plasma exposure can “super-saturate” the near-surface region of materials with low H solubility, but any H inventory above the natural solubility of the PFC must occupy a trap or it will diffuse freely until it is released from a surface.

Hydrogen trapping occurs in an energy well within the material. These energy wells can be vacancies, defects such as grain boundaries or dislocations, voids, or bubbles. A trapped hydrogen, by definition, is *not* free to diffuse in the material, it remains in the trap until sufficient thermal energy is provided for it to escape the energy well. Hydrogen trapping is then defined by the trap density (traps/unit volume), C_T , and the depth of the trap energy well, E_T . However, since there can be several different types of traps, each with their own C_T and E_T values, the trapping properties can quickly become difficult to interpret and predict. Also, trap density is not necessarily a constant value nor constant with depth into the surface. Additional trap sites can be created in a material due to radiation damage or stresses and trap sites can be removed from a material by annealing at high temperatures. Traps can also combine to form new traps with different C_T and E_T values, such as vacancy clustering to form voids in metals [5]. There are two different trap types to consider as well. Traps can be saturable, such that they can only accommodate a certain amount of hydrogen as in the case of vacancies or defects. Unsaturable traps, such as bubbles, can accommodate increasing amounts of hydrogen depending on the hydrogen pressure that can be contained within the bubble, which is a function of hydrogen density itself [5].

Diffusion is the movement of an interstitial atom from one interstitial site to another. Due to its small physical size (Bohr radius ~ 50 pm), hydrogen is typically mobile in materials, especially metals, although there are exceptions, such as C, where H diffusion is low. Fick’s Law tells us that particles want to diffuse down their density gradient, so in order for diffusion to occur we must first have a density gradient. For a PFC exposed to a plasma, a very large H density gradient is provided by ion implantation. Plasma ions of a given energy will deposit themselves into the PFC up to a known depth, called the implantation depth. As long as there is a high flux plasma to provide a source of incident ions there will be a large H density gradient peaked at the hydrogen implantation depth, so H will proceed to diffuse out from the implantation depth in all directions. Diffusion rate, $D \left[\frac{m^2}{s} \right]$, is determined by the temperature and specific properties of the material

and is defined by equation 1.2.

$$D = D_o \exp\left(\frac{-E_D}{k_B T}\right) \quad (1.2)$$

D_o is the constant diffusion coefficient and E_D is the activation energy for diffusion. These values are unique for each material. Much like solubility, eq. 1.1, diffusion is strongly dependent on temperature, with D always increasing with temperature. There are other factors that can affect hydrogen diffusion. It has been shown that very small amounts of impurities in a material [6, 7] or trap sites [8] can reduce the diffusion of hydrogen, while the presence of grain boundaries has been shown to accelerate hydrogen diffusion [9]. Neutron irradiation has also been shown to reduce diffusion by small amounts [10]. Diffusion rates and solubility are commonly derived from permeation rates through the relationship, $P = DS$, where the permeation is typically measured by a gas permeating through a thin foil. However, thin films of oxides or other impurities typically form on surfaces and these films of impurities may cause the diffusion in the near-surface and bulk regions to have different values. This can lead to a wide range of experimentally determined diffusion rates for a single material due to differences in surface conditions.

Dynamic retention is strongly affected by the rate limiting processes during an ion implantation. Solubility, trapping, diffusion, and surface recombination all go to determining the dynamic retention. The hydrogen concentration in the PFC can be found as a function of position and time by solving the continuity equation.

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial r^2} + S(r, t) \quad (1.3)$$

C is hydrogen concentration (H/unit volume), D is the diffusion rate, and $S(r, t)$ is the hydrogen source term. During a plasma discharge, determining the steady-state concentration of H simplifies eq. 1.3, and allows for the concentration to be modeled by conservation of flux. In steady-state ($\frac{\partial}{\partial t} = 0$), the implanted flux [$\text{m}^{-2}\text{s}^{-1}$], Φ_i must be equivalent to the recycled flux, Φ_J (flux of H emitted from the front surface) plus the permeated flux, Φ_p (flux of H emitted from the back surface).

$$\Phi_i = \Phi_J + \Phi_p \quad (1.4)$$

Φ_J and Φ_p are determined by surface recombination or diffusion, whichever one is the limiting process [11, 12].

$$\Phi_J = k_f C_f^2 = D \frac{C_r - C_f}{r_{imp}} \quad (1.5)$$

$$\Phi_p = k_b C_b^2 = D \frac{C_r - C_b}{L} \quad (1.6)$$

$k \left[\frac{m^4}{s} \right]$ is the rate constant for surface recombination, r_{imp} is the implantation range of the ions, and L is the total thickness of the PFC. The subscripts f , r , and b refer to the front face, implanted region and back face of the PFC respectively.

Figure 1.1 The model for steady-state hydrogen concentration during a plasma exposure or ion implantation.

Some assumptions, such as $r_{imp} \ll L$, and neglecting energy straggling on implantation depth (i.e. one assumes a delta-function, $\delta(r)$, for the implantation depth) have been made to simplify eqs.1.5-1.6. It was also assumed that the diffusion rate, D , was constant throughout the entire sample even though there is evidence that diffusion is not necessarily the same in the front and back sections of the PFC [11, 13].

To solve for the steady-state concentrations, C_f , C_{imp} , and C_b , for eqs.1.4-1.6, it is convenient to define some dimensionless parameters [12, 11].

$$u = C_f \sqrt{\frac{k_f}{\Phi_i}} \quad (1.7)$$

$$v = C_b \sqrt{\frac{k_b}{\Phi_i}} \quad (1.8)$$

$$\alpha = \frac{r_{imp}}{L} \quad (1.9)$$

$$\beta = \sqrt{\frac{k_f}{k_b}} \quad (1.10)$$

$$W = \frac{r_{imp} \sqrt{k_f \Phi_i}}{D} \quad (1.11)$$

It is important to note that $\alpha \ll 1$ in plasma situations ($r_{imp} < 10 \text{ nm}$, $L > 1 \text{ mm}$) and if the assumption that $L \gg \frac{D}{\sqrt{k \Phi_i}}$ can be made then the concentrations can be accurately approximated.

$$C_f = \sqrt{\frac{\Phi_i [1 - \alpha (1 + 1/W)]}{k_f}} \quad (1.12)$$

$$C_r = \sqrt{\frac{\Phi_i}{k_f}} [W + 1 + \beta \sqrt{\alpha (1 + 1/W)}] \quad (1.13)$$

$$C_b = \sqrt{\frac{\Phi_i \alpha (1 + 1/W)}{k_b}} \quad (1.14)$$

All concentrations are dependent on W , so the value of W can be used to determine the limiting processes for the front and back surfaces. If $W > 1$ then the front and back surfaces are both diffusion-limited processes (DD-regime). If $\alpha \beta^2 < W < 1$ then the front surface is recombination limited and the back surface is diffusion-limited (RD-regime). If $W < \alpha \beta^2$ then both the front and back surfaces are recombination limited (RR-regime) [12]. Notice that this formalism does not allow for a DR-regime and assumes constant diffusion throughout the entire sample. A slightly more complex formalism splits W into three parameters, U , V , and X , and allows for different diffusion rates in the front and back of the PFC ($D_f \neq D_b$) and the possibility of a DR-regime [11].

$$U = \frac{r_{imp} \sqrt{k_f \Phi_i}}{D_b} \quad (1.15)$$

$$V = \frac{D_b(k_f + k_b)}{Lk_b\sqrt{k_f\Phi_i}} \quad (1.16)$$

$$X = \frac{D_f D_b}{rLk_b\Phi_i} \quad (1.17)$$

Now the RR-regime is defined when $V > 1$ and $X > 1$, the RD-regime when $U < 1$ and $V < 1$, the DD-regime when $U > 1$ and $UVX < 1$, and finally the DR-regime when $UVX > 1$ and $X < 1$ [11].

It is clear that surface recombination plays a strong role in the dynamic inventory. It has been shown that deuterium can be re-emitted from the surface in atomistic form but only for temperatures >1200 K [14]. However, these temperatures are not relevant for this study nor for most steady-state fusion reactors. The hydrogen surface recombination rate is dependent on the materials just like diffusion and solubility. However there is more uncertainty surrounding surface recombination. Baskes has developed a model for an Arrhenius relation for the surface recombination coefficient, k , that has the subsurface hydrogen participating in the desorption process [15]. Pick and Sonnenberg developed a model based on the loss of hydrogen from solution and how that related to the incidence of molecules from a gas phase [16]. As an example of the range of scatter for recombination rates, these two models differ by 4-6 orders of magnitude, depending on temperature, when predicting the surface recombination coefficient for iron [17]. The model that appears to consistently reproduce results over a wide range of temperatures and metals, is by Wampler [17, 18]. This model is based on the assumption that the release of hydrogen is recombination limited and that the recombination sites and solution sites are in quasi-equilibrium. The model yields an Arrhenius relation for the surface recombination coefficient, k , similar to that of diffusion (see eq. 1.2) or solubility (see eq. 1.1).

$$k = k_o \exp\left(\frac{2(E_{rc} - E_B)}{k_B T}\right) \quad (1.18)$$

k_o is a material dependent constant, E_B is an energy barrier to recombination, and E_{rc} is the energy of an H atom in a recombination site [18]. Extra care must be taken when measuring the surface recombination coefficient for materials since there is a wide range of factors that can have strong effects on the surface recombination. It has been shown that even small amounts of

oxides on a surface can drastically reduce surface recombination [17, 19, 20]. It has also been observed that surface defects, such as those produced by radiation damage, can strongly catalyze surface recombination [21]. Crystal orientation also plays a weak role in surface recombination [17]. Controlling all of these factors in an experiment or creating a model that encompasses all of them is a difficult task. For a PFC, where there is a high chance of radiation damage and surface contamination, it is important to be able to measure the surface recombination rate and its effects directly rather than trying to predict it with a model.

1.3 Motivation for Thesis

Metals, specifically molybdenum (Mo) and tungsten (W), are a common choice for PFC materials. Both these metals have high melting points, good mechanical strength, excellent sputtering resistance, and low solubility for hydrogen. The low solubility is thought to result in very low hydrogenic retention in these metals and alleviate the concerns about tritium retention in next-generation fusion devices. However, a recent campaign on the Alcator C-Mod tokamak at the Massachusetts Institute of Technology, has shown that hydrogenic retention in high-Z materials can be significant.

Alcator C-Mod is a compact, high field, divertor tokamak ($\sim 1 \text{ m}^3$ plasma volume, major radius $\sim 0.6 \text{ m}$, plasma radius $\sim 0.2 \text{ m}$), which operates at high magnetic field ($\sim 5 - 8 \text{ T}$), high plasma density ($1 - 5 \times 10^{20} \text{ m}^{-3}$), high parallel heat loads ($\sim 0.5 \text{ GW/m}^2$), and high ion flux density ($\leq 10^{23} \text{ m}^{-2} \text{ s}^{-1}$ in the divertor). This makes Alcator C-Mod useful for re-creating ITER-like plasma edge conditions. Alcator C-Mod uses Mo as their only “bulk” ($\sim 1 \text{ cm}$ thick) PFC material. The Mo PFC tiles are inertially cooled via mechanical attachment to the structure and vessel of the tokamak. The Mo is intermittently covered by a thin film (10-100 nm) of boron (B) using an Electron Cyclotron Discharge Cleaning plasma discharge with 10% diborane gas (B_2D_6) and 90% helium gas inside the device [22]. The B getters oxygen chemically and temporarily covers the Mo surface from the plasma. The low-Z boron coating helps lower plasma impurity radiation losses and this improves plasma confinement [22]. In next-generation, long pulse diffusion devices, these thin films are expected to be sputtered away early in the discharge so the PFC will be bare

metal, unlike the short pulses (1-3 seconds) in Alcator C-Mod. To create a “clean” metal wall in Alcator C-Mod, all boron-nitride tiles were replaced with Mo tiles, all removable Mo tiles (limiters, upper divertor) were removed and ultrasonically cleaned, and non-removable tiles and surfaces (inner divertor, stainless steel walls) were wiped with deionized water to remove deposited boron films. After the cleaning there was typically 10-30% B/Mo distributed through the first micron of the surface, as opposed to before cleaning where there was typically 95-100% B coverage of the surface region [22].

Alcator C-Mod is able to measure the amount of deuterium retained in the walls during a plasma discharge through two methods. The first, and most accurate, method is to close the pump gate valves before the discharge until ~ 5 minutes after the discharge when the pressure inside the vessel has reached equilibrium, as measured by constant vessel pressure. The recovered deuterium and hydrogen is characterized by the vessel pressure with the pump valves closed. The second method relies on the fact that the pumping speed of the torus pumps is well-known as a function of pressure. So the amount of deuterium gas pumped out of the vessel can be calculated and compared to the amount of gas that was injected into the vessel during the discharge. The difference in these values is the net retention or depletion of the wall inventory per discharge [22].

For the “clean” Mo wall, approximately half of the injected deuterium gas was not recovered, and therefore resides in the wall. With repeated discharges the amount of deuterium gas lost decreased to $\sim 30\%$ per discharge, but this amount is still much higher than expected for a Mo wall (see Fig. 1.2).

There were no signs of the deuterium inventory in the Mo wall saturating over the course of 10 discharges before the first boronization was applied to the Mo [23]. Figure 1.3 shows that, for repeated plasma discharges avoiding disruptions, the retained D fluence in the wall scales linearly with the incident D fluence on to the wall at a rate of 0.35 %. If all of these shots are summed together and a cumulative inventory is tracked, this also reveals a linear dependence for retention, but in this case the dependence is 0.75 % retention rate (see Fig. 1.4). The difference in retention rate between these two plots has to do with how the D ion flux to the wall is treated [23]. The linear nature of the dependence indicates the retention is not saturating with increasing incident fluence

Figure 1.2 Deuterium retention for a series of discharges on Alcator C-Mod with bare Mo walls. Plasma parameters for all discharges were $I_p = 1\text{MA}$, $\bar{n}_e = 1.6 \times 10^{20}\text{m}^{-3}$, and $\Delta t_{\text{Discharge}} = 2.25\text{s}$.

Figure 1.3 The retained deuterium per shot as a function of deuterium fluence to the “clean” Mo wall in Alcator C-Mod. The different fluences were achieved by different discharge durations ranging from 1 - 2.5 s.

Figure 1.4 The retained fluence as a function of incident D ion fluence for cumulative shots through out an experimental run with "bare" Mo walls in Alcator C-Mod.

and is not limited by diffusion. It is critical that this result be understood if ITER is to have an all-metal wall. There are 100 g of T injected into ITER for each discharge, if 30% of the T is lost to the walls then it will only take 10-12 discharges to reach ITER's T-inventory safety limit of 350 g [1, 2].

There has been a great deal of laboratory work done on the hydrogenic retention of refractory metals such as Mo and W, however experience and measurement of H retention with all-metallic walls in a tokamak is extremely limited. Furthermore, the tokamak surfaces are very difficult to access, therefore the mechanisms which are involved in the retention must be indirectly inferred from the phenomenology of the retention rates. Straightforward extrapolation of retention from laboratory measurements, which are primarily ion beam and gas permeation experiments, to the complexity of tokamak exposures, does not appear adequate to explain the Alcator C-Mod results. It is essential to examine hydrogenic retention in conditions similar to those found in a tokamak, and to gain a better understanding of the dynamics of retention, trapping, diffusion and surface recombination in a tokamak environment.

Chapter 2

Background

2.1 Molybdenum as a PFC

Molybdenum (Mo) is currently used as the PFC material in the Alcator C-Mod device and several limiter tokamaks such as the Frascati Tokamak Upgrade (FTU) and the Tokamak Research Institute for Applied Mechanics (TRIAM) [22]. Mo is a refractory metal, and as such, has many of the properties that are desired in an ideal PFC (see section 1.1). An extremely high melting point ($T_{melt} = 2883K$) and excellent thermal conductivity ($K = 142W/mK$ at $298K$) make the thermo-mechanical properties of Mo desirable in a PFC. Mo is also very hard and strong, which makes it resilient to mechanical and thermal stresses and strains even at elevated temperatures. Table 2.1 lists a number of physical, mechanical and thermal properties of Mo and compares them to W, another refractory metal typically used in fusion applications [24, 25]. It is seen in Table 2.1 that Mo is slightly cheaper and much more ductile, meaning more easily machined, than W. However, W has a higher melting point, which makes it more resilient to high transient heat loads and also has more favorable neutron activation characteristics.

Mo also has a high atomic number and surface binding energy (~ 6.8 eV), which makes it resilient to physical sputtering but also a more perturbing plasma impurity since it is a high-Z element. Operating Alcator C-Mod with bare Mo PFC, it was not possible to obtain a high quality core plasma energy confinement because the Mo impurities radiate too much energy from the core plasma [22]. To minimize the amount of Mo introduced into the plasma, Mo PFC are often covered with a low-Z coating such as boron in the case of Alcator C-Mod. The boron prevents Mo from being sputtered into the plasma and also acts as an oxygen getter to remove impurities already

Properties	Molybdenum	Tungsten
Atomic Number	42	74
Atomic Weight	95.54 amu	183.85 amu
density	10.22 g/cm ³	19.254 g/cm ³
Crystal Structure	BCC	BCC
Lattice Constant (a)	0.31468 nm	0.31652 nm
Melting Point	2883 K	3683 K
Boiling Point	5833 K	5973 K
Recrystallization Temperature	1453 K	1473 K
Specific Heat Capacity	276 J/kg·K	138 J/kg·K
Linear Coefficient of Thermal Expansion	$4.9 \times 10^{-6} \text{ K}^{-1}$	$4.5 \times 10^{-6} \text{ K}^{-1}$
Thermal Conductivity	142 W/m·K	155 W/m·K
Modulus of Elasticity	320 GPa	400 GPa
% Elongation (Ductility)	25	2
Yield Strength	500 MPa	760 MPa
Tensile Strength	630 MPa	960 MPa
Relative Cost	143	166

Table 2.1 Selected physical, thermal, and mechanical properties of Mo and W. All values are taken at room temperature (298 K). Relative cost is the cost by weight relative to A36 plain carbon steel.

found in the plasma. The boron film will also be sputtered from the PFC but the plasma is much more tolerant to a low-Z impurity such as boron ($Z=5$).

The chemical activities of Mo with hydrogen and common plasma impurities such as oxygen and carbon are also of interest. Mo does not commonly form a hydride, although there is evidence of hydride formation in experiments [26], but it can form oxides (MoO_2 , Mo_2O_3 , Mo_2O_5) at elevated temperatures. Mo can also form carbides (MoC , MoC_2) which is more of a concern if there are both C and Mo PFC in a tokamak.

The most important aspect of Mo for fusion use is the behavior of hydrogen and hydrogenic isotopes in Mo. Despite many studies examining this topic, there is still a great deal of uncertainty in our understanding of the mechanisms of H trapping, permeation and re-emission in Mo. Because of the similarities in structure and properties between Mo and W, results from work performed on W can also be drawn upon to resolve the mechanisms of hydrogenic transport.

2.2 Hydrogenic Transport in Mo

The mobility of hydrogen in Mo is of great importance for both dynamic and equilibrium retention. Hydrogenic transport is dictated by solubility, diffusion, permeability and surface re-combination.

Permeability studies of H in Mo or W are of great use since the permeability of a metal can also lead to the solubility and diffusion rate through the relation $P = SD$. Permeability studies use thin samples (5-100 μm thickness), which are much thinner than PFC tiles found in a tokamak. Permeability studies are typically in the RR-regime, whereas a PFC in a tokamak (assuming the tokamak is not running with hot walls) will operate in the RD-regime (see sec. 1.2). The data for the solubility and diffusivity of hydrogen in Mo spans 5 decades and has a large scatter and uncertainty (see figures 2.1-2.2). The thermal history and inherent impurities in the samples are thought to also be responsible for the scatter in data. Also, the scatter is thought to be due to the bcc structure of the metal and its high melting point, although the reasons for this are not made clear [4]. Most of the older data was taken with samples made by powder sintering which might have introduced additional impurities or lattice defects. A review of this topic was written 15 years ago by K.L. Wilson, but most of the experimental work done of diffusion and solubility of Mo was performed before 1991, so the review remains valuable and accurate despite its age [4]. Some of the experiments will be discussed in detail but a more thorough collection of the data can be seen in figure 2.1 [27, 28, 29, 30, 31, 10, 32, 33, 34, 35] and figure 2.2 [36, 34, 27, 37, 10, 32, 33, 31].

Caskey et al. examined the permeability of deuterium gas through a 127 μm thick 99.8 % Mo foil prepared by electron beam melting [34]. The permeation rate was monitored as a function of

Figure 2.1 A collection of experimental fits for the diffusivity of hydrogen/deuterium in Mo as a function of temperature.

Figure 2.2 A collection of experimental fits for the solubility of hydrogen/deuterium in Mo as a function of temperature.

time over a temperature range of 523-730 K. Their permeation data is fit by the Arrhenius relation:

$$P \left[\frac{\text{mol}}{m \cdot s \cdot \sqrt{\text{MPa}}} \right] = 3.22 \times 10^{-4} \exp \left(\frac{-0.863 \text{eV}}{kT} \right) \quad (2.1)$$

The diffusion of deuterium in Mo was determined from the evolution rate of the permeability from the time the deuterium was first introduced until the permeability reached steady-state (labeled as “rising”) and from the time the deuterium was removed until the permeability reached equilibrium (labeled as “declining”).

$$D_{\text{declining}} \left[\frac{m^2}{s} \right] = 2.73 \times 10^{-4} \exp \left(\frac{-0.84 \text{eV}}{kT} \right) \quad (2.2)$$

$$D_{\text{rising}} \left[\frac{m^2}{s} \right] = 5.75 \times 10^{-6} \exp \left(\frac{-0.72 \text{eV}}{kT} \right) \quad (2.3)$$

The diffusion rate measured from the “rising” permeability is consistently lower than the diffusion rate measured from the “declining” permeability. The “declining” diffusivity is thought to be closer, but still slightly lower, than the true lattice diffusivity. The solubility can be calculated directly from the permeability and diffusivity (using the “declining” diffusivity) through the relation $P = DS$.

$$S \left[\frac{\text{mol}}{m^3 \sqrt{\text{MPa}}} \right] = 1.18 \exp \left(\frac{-0.023 \text{eV}}{kT} \right) \quad (2.4)$$

Tanabe et al studied the permeability of >99.999% pure hydrogen gas through a 99.9 % pure Mo 0.1-1 mm thick disc produced by powder metallurgy [31]. The disc was annealed at 1200 K for 2 h before any experiments were performed. The temperature range for experiments was 500-1100 K. The diffusivity was determined by the “rising” and “declining” data but only the “declining” data was presented since the “rising” method was very sensitive to surface condition. The solubility was obtained through the $P = DS$ relationship.

$$P \left[\frac{\text{mol}}{m \cdot s \cdot \sqrt{\text{MPa}}} \right] = 1.4 \times 10^{-4} \exp \left(\frac{-0.63 \text{eV}}{kT} \right) \quad (2.5)$$

$$D \left[\frac{m^2}{s} \right] = 4.0 \times 10^{-8} \exp \left(\frac{-0.23 \text{eV}}{kT} \right) \quad (2.6)$$

$$S \left[\frac{\text{mol}}{m^3 \cdot \sqrt{\text{MPa}}} \right] = 3.3 \times 10^3 \exp \left(\frac{-0.39 \text{eV}}{kT} \right) \quad (2.7)$$

While the permeability values for Caskey and Tanabe (eqs. 2.1 and 2.5 respectively) are in relatively good agreement, the diffusivity (eqs. 2.2 and 2.6) and solubility (eqs. 2.4 and 2.7) are quite different. The diffusivity and solubility of Tanabe et al appear to agree better with other experiments (see figures 2.1 and 2.2) than the results from Caskey et al. The Tanabe experiment made an effort to use ultra-pure hydrogen gas for their permeability studies. When they added small amounts (<80 appm) of water to their hydrogen gas they noted a small decrease in diffusivity [31]. Perhaps this effect was more pronounced for the Caskey results if there were significant impurities in their deuterium gas. This is a perfect example of how two seemingly similar experiments yield very different results when trying to determine the diffusivity of hydrogen in Mo.

Tanabe et al also performed ion-driven permeability studies of Mo where 30 keV D⁺ ions were implanted into the metal rather than neutral gas permeation [35]. The Mo sample was a 99.99 % Mo 100 μ m thick foil. The foil was annealed at 1273 K for 2 h before being implanted with the D⁺ ions. Experiments were performed from 500-1000 K. The diffusivity was taken from the evolution of the permeation rates similar to the procedure followed by Caskey et al [34].

$$D \left[\frac{m^2}{s} \right] = 3.2 \times 10^{-6} \exp \left(\frac{-0.57 eV}{kT} \right) \quad (2.8)$$

It was noted that the permeation rose quickly (1-5 s) to its maximum and then gradually decreased over the remainder of the exposure (>200 s). This gradual decay of the permeation rate also means the diffusion rate will also decrease with time. Eq. 2.8 represents the maximum diffusion rate observed in the experiments. This gradual reduction in diffusion is explained as possibly evidence of radiation induced defects (i.e. defects caused by the ion beam irradiation) diffusing into the bulk of the foil and inhibiting diffusion [35]. This permeation “spike” has been observed in other experiments and alternative explanations such as enhanced surface recombination due to physical or chemical sputter cleaning of surface impurities [13], or enhanced surface recombination due to radiation-induced surface defects [21] have been proposed. Because this “spike” has never been seen for neutral gas permeation experiments, it can be concluded that ion damage of some sort is causing this effect. This is another important indication that the retention characteristics are affected by the nature of the H/D introduction to the material.

Katsuta et al determined the diffusivity and permeability of hydrogen in Mo by the time-lag method for a temperature range of 833-1193 K [33]. This method calculates the permeability and diffusivity based on the slope of increasing permeated hydrogen versus time. This allows for the permeability and diffusivity to be calculated within the first few seconds of an experiment, hopefully before any surface effects start to accumulate. There were four samples examined: (1) 0.18 mm thick Mo foil formed by electron beam melting, (2) the same as (1) except with a 30 min. anneal at 1573 K, (3) the same as (1) except with a thin (~ 200 nm) coating of palladium metal, and (4) 0.19 mm thick Mo foil formed by powder sintering. Despite all the different treatments, all samples yielded very similar permeation, diffusion, and solubility rates.

$$P \left[\frac{\text{mol}}{\text{m} \cdot \text{s} \cdot \sqrt{\text{MPa}}} \right] = 1.23 \times 10^{-4} \exp \left(\frac{-0.77 \text{eV}}{kT} \right) \quad (2.9)$$

$$D \left[\frac{\text{m}^2}{\text{s}} \right] = 2.39 \times 10^{-8} \exp \left(\frac{-0.11 \text{eV}}{kT} \right) \quad (2.10)$$

$$S \left[\frac{\text{mol}}{\text{m}^3 \sqrt{\text{MPa}}} \right] = 6.02 \times 10^3 \exp \left(\frac{-0.66 \text{eV}}{kT} \right) \quad (2.11)$$

Again, the permeability is in good agreement but the activation energy, E_D (see eq. 1.2), is 2-7 times lower than all other values in the literature. It was reasoned that previous experiments most likely had a surface oxide present that increased the measured diffusivity. It is also noted that theoretically calculated activation energies for BCC metals based on a simple elastic model yield an activation energy for Mo diffusion of 0.12 eV [33], which is in close agreement with equation 2.10, and that the annealed sample had very similar diffusivity as the non-annealed samples, which would indicate that trapping plays little or no role in diffusion.

For W, Frauenfelder published a comprehensive study of the diffusion and solubility of hydrogen in W in 1969 [38]. The diffusion and solubility of hydrogen in W were measured by degassing a W cylinder that was “loaded” by hydrogen by baking in a hydrogen rich environment. The degassing rates yielded values for diffusivity and solubility over a temperature range of 1100-2400 K.

$$D \left[\frac{\text{m}^2}{\text{s}} \right] = 4.1 \times 10^{-7} \exp \left(\frac{-0.39 \text{eV}}{kT} \right) \quad (2.12)$$

$$S \left[\frac{\text{mol}}{\text{m}^3 \cdot \sqrt{\text{MPa}}} \right] = 1.47 \times 10^3 \exp \left(\frac{-1.04 \text{eV}}{kT} \right) \quad (2.13)$$

These are by far the most referenced values for diffusivity and solubility of hydrogen in W despite the fact they are over 35 years old. W does not have nearly the scatter of data as is seen for Mo, but this may be due to a lack of data to compare. Zakharov et al also investigated diffusivity and solubility of W and got very different results as compared to Frauenfelder [32]. Zakharov reported an extremely high activation energy for diffusion, $E_D = 1.07 \text{eV}$, and an extremely low heat of solution for solubility, $E_S = 0.03 \text{eV}$, which is exactly opposite of Frauenfelder who had a high E_S , and a much lower E_D . It is unclear why Frauenfelder's results are often referenced in articles but Zakharov's work is seemingly ignored.

When considering diffusion from implanted ions, other factors must be considered. If the energy of the ions is high enough, then trap sites can be produced and these traps will inhibit diffusion. The effects of trap sites on diffusion was considered by Shu et al, and an equation was presented such that an effective diffusion rate can be derived if the trapping mechanisms and characteristics are well known [39].

$$D_{eff} = \frac{D_l}{1 + (C_T/C_l) \exp(E_T/kT)} \quad (2.14)$$

D_l is the lattice diffusivity, $C_T \left[\frac{\text{traps}}{\text{m}^3} \right]$ is the trap density, $E_T \text{ [eV]}$ is the trap binding energy, and C_l is the density of interstitial lattice points. One can also solve eq. 2.14 for the trap energy if the lattice diffusivity and trap density is known and the effective diffusivity, D_{eff} , can be measured. For lower ion energy implantations diffusivity can still be affected. Zakharov et al proposed that at low ion energies, hydrogen atoms can combine with Mo self-interstitial atoms (SIA) to form H-SIA complexes [40]. These H-SIA complexes have a very low activation energy ($\sim 0.2 \text{eV}$) and have access to short diffusion paths as they travel through the lattice in a dumbbell configuration. This results in enhanced diffusion of hydrogen in Mo for low energy ion implantation. When these complexes decay they can leave trap sites, potentially very deep in the Mo. So this could be considered an enhanced trap diffusion as well. It has also been shown that the additions of boron and carbon impurities to Mo lower the diffusivity [41, 6]. This effect is thought to be due to the

additional trap sites provided by the introduced impurities, which according to eq. 2.14, would reduce the effective diffusivity.

Trap diffusion is another important topic to consider. Because the hydrogenic solubility of refractory metals is so low, the hydrogen inventory in the bulk of a PFC will be negligible unless there is significant trap concentration beyond the interstitial solubility. Tanabe et al explained the permeation “spike” seen for ion-driven permeation as evidence for hydrogen traps diffusing from the implantation zone into the bulk of the material [35]. A study of depth-resolved deuterium retention in Mo by Nagata et al. showed that the deuterium concentration extended well past the implantation depth moved deeper into the sample with increasing sample temperature [42]. This would indicate D traps diffusing deeper into the sample and that this trap diffusion rate is also dependent on sample temperature. Trapping will be discussed further in sec. 2.3 and trap migration will be discussed further in sec. 2.4.

Most surface recombination studies are performed on nickel, iron or steels. For hydrogen in Mo, no previous work that measured the surface recombination rate directly was found. As mentioned in section 1.2, the surface recombination rate for pure Mo is very difficult to measure. Even if it were known, it would not be applicable to a PFC study where the surfaces are constantly changing. It is valuable to understand some of the methods of measuring surface recombination since each experiment should measure their own value for R , to get the most accurate and applicable numbers. There is one study by Anderl et al. measuring the surface recombination rate of H in W [43]. If the traps in the tungsten are assumed to be saturated and the implantation depth is much smaller than the sample thickness, then the surface recombination rate can be measured by monitoring both the permeated and the re-emitted fluxes.

$$k = \frac{D^2}{2L^2} \frac{\Phi_J}{\Phi_p^2} \left(1 - \frac{r_{imp}}{L} \frac{\Phi_J}{\Phi_p} \right)^{-2} \quad (2.15)$$

For their measurements, the diffusion rate was taken from Frauenfelder [43, 38]. Three samples were measured for a temperature range of 610 - 823 K. One sample was left unannealed and the other two samples were annealed at 1273 K and 1673 K respectively. The unannealed sample had the highest recombination rate and the two annealed samples were very similar (see Fig. 2.3)[43].

Figure 2.3 Recombination rate for hydrogen in annealed and unannealed W samples.

The easiest way to obtain the surface recombination rate is to measure the hydrogen inventory during an exposure that is known to be recombination limited. If the incident ion flux is known then the change in inventory with and without the source of hydrogen can be used to solve for k .

$$k = \frac{2\Phi_i}{(\Delta n)^2} \quad (2.16)$$

The problem with this method is that measuring the dynamic H inventory of a PFC is very difficult, if not impossible for most experiments. However, for an experiment that was specifically designed to investigate the dynamics of plasma-surface interactions, this should not be an issue, so recombination rates for samples should be readily attainable.

2.3 Hydrogenic Trapping in Mo

Because the solubility of hydrogen in Mo is so low, hydrogenic trapping is critical in determining the equilibrium retention of Mo. In fact, in a great deal of the literature the concepts of trapping and retention are used interchangeably. Since equilibrium retention is considered the most critical for issues such as tritium retention, there is an abundance of literature on hydrogenic trapping in both Mo and W.

The most common method of analyzing hydrogenic trapping is with thermal desorption spectroscopy (TDS). After a sample has been implanted with hydrogen and trap sites have been filled, the trapped hydrogen requires energy to escape its trap site and diffuse out of the sample. This energy can be provided by heating the sample. TDS ramps up the temperature of the sample at a known rate. While the temperature increases a residual gas analyzer (RGA) mass analyzes the gas being released from the sample. By correlating the rate of the release of hydrogen at a particular temperature conclusions can be made as to the energy of the traps based on an Arrhenius relationship, the trap concentration and total hydrogen retained. Ion beam analysis (IBA) can also be used to determine the relative concentration of deuterium as a function of depth in the surface. The ability of IBA to determine the location of the deuterium within a surface can reveal the role of diffusion in trapping and it is also useful for applications such as tritium recovery methods.

While there are several studies that use IBA to study hydrogenic retention and trapping in W [13, 44, 45], there are fewer studies using IBA to study Mo [42, 45]. Nagata et al implanted a thin (5 μm) Mo foil with a Zr film on the backside of the foil. The foil was implanted with 5 keV D⁺ ions for temperatures of 300-600 K. The Zr film on the backside of the foil acted as a permeation barrier and “captured” the hydrogen as it permeated through the thin Mo foil. IBA was used to measure the deuterium concentration for the entire thickness of the foil, including the Zr film.

Several studies have been made to determine the binding energies of hydrogen atoms in vacancies, thought to be the most common trap site in Mo, using a variety of techniques including TDS [46, 47, 48, 49, 50]. Typical trap energies ranged from 1.0-1.4 eV. This scatter in energy may be a result of different vacancy types or different methods of vacancy formation. The experiment most closely recreating a tokamak plasma environment was performed by Causey et al [46], where Mo was exposed to a Penning deuterium discharge resulting in a high flux of 600 eV D⁺ ions. These experiments were conducted at elevated temperatures (573-773 K) but were shown to somewhat agree with lower temperature measurements made by Wilson on TZM, a Mo alloy [46, 51]. The Mo samples were exposed to deuterium fluences of 5.4×10^{23} D/m² and then thermally desorbed to a temperature of 1373 K with a temperature ramp of 1.67 K/s. At 573 K it was found that using trap energies of 1.4 eV and 2.1 eV gave the best fits when using the DIFFUSE code. At higher

exposure temperatures (>673 K) the 1.4 eV traps and the higher energy traps shifted upward to 2.9 eV, a very high value for trap energy. The 1.4 eV trap was thought to be radiation-produced vacancies and it was suggested that the 2.9 eV traps were evidence of bubble or blister formation and chemisorption of deuterium on the inner surfaces of the bubble. The retained fraction of incident deuterium decreased from 10^{-4} to $\sim 3 \times 10^{-6}$ with increasing temperature (573-773 K). However retained fraction is somewhat misleading in terms of retention properties if the sample is not saturated. Since trap concentrations as high as 1.5×10^{-2} traps/Mo were found with the DIFFUSE fits, this corresponds to $\sim 2 \times 10^{24}$ traps/m² in the 2 mm thick sample. The retained fraction of 10^{-4} translates to 5×10^{19} D/m² retained, so clearly this sample is not saturated.

In fact the saturation fluence for a material is a critical value to know for hydrogenic retention and trapping studies. *For all the fluence studies of retention, a saturation fluence of Mo has not been observed.* This is most effectively shown by Haasz et al [52]. In their work, an ion beam was used to implant 1 keV D⁺ ions into Mo, W, and Be for fluences ranging from $10^{21} - 10^{25}$ D/m² at room temperature and the total amount of retained deuterium was measured by TDS. The Mo sample was 100 μ m thick and the W and Be samples were 25 μ m and 130 μ m thick respectively. Their data shows that at low fluences, Mo has the lowest amount of retained deuterium as compared to W or Be. However, while the amount of retained deuterium for W and Be appears to begin saturating at a incident fluence of $\sim 10^{22}$ D/m² while the Mo shows no signs of saturating. At an incident fluence of $\sim 10^{25}$ D/m², the retained deuterium for W and Mo are roughly equal at $\sim 6 \times 10^{20}$ D/m², but the Mo retained deuterium is still increasing monotonically (but less than linearly) while the W retention has saturated [52]. Sakamoto et al have also observed the deuterium retention in W to begin to saturate at fluences of $10^{21} - 10^{22}$ D/m² while the retention in Mo continued to rise [53]. The overall retention seen by Sakamoto was much greater than that seen by Haasz but this could be due to the energy of the incident ions or a lack of pre-annealing by Sakamoto. Sakamoto implanted the samples with 8 keV D⁺, which would translate to a higher trap production rate. Yamaguchi et al also observed a linear increase of retained deuterium as a function of incident fluence at low (<400 K) temperatures although for a much lower fluence range ($10^{19} - 10^{21}$ D/m²) [54].

The lack of saturation indicates one of two possibilities. Either that the deuterium implantation in Mo is producing available traps faster than they can be filled, or that Mo has a much higher natural trap density than W. Since retention in Mo is lower than retention in W for low incident fluences, it would appear that the natural trap density of Mo might actually be *less* than W, which is measured to be ~ 50 appm [43]. It is doubtful that a single, low-energy deuterium ion could produce more than a single trap site, but the type of traps being created may be of great importance. If there are blisters or bubbles formed in the material then these are considered “unsaturable” traps and each bubble could contain huge numbers of deuterium ions that have either chemisorbed to the inner surface of the bubble or have recombined on the inner surface of the wall and are now a molecule trapped in the void of the bubble. These bubbles can have very powerful effects on the hydrogenic trapping properties of a material so it is critical that their creation and growth conditions be well understood.

An excellent review of hydrogen bubble formation in metals is given by Condon and Schober [5]. In this review, three main mechanisms for bubble or void formation are given. Blistering is defined as plastic deformation near the surface and is caused by the implantation of hydrogen at a rate faster than which it can be removed. The implanted hydrogen then nucleates into small bubbles and pressure in the bubbles can mechanically deform the bubble further and form a blister. Dislocation loop punching is the formation of bubbles in the bulk of the metal. Again, hydrogen collects in a void in the bulk and once sufficient pressure has been built up the void will create a dislocation loop to create more volume to relieve pressure. Vacancy clustering is the collection of vacancies to create a void in the bulk of the material. Migration of vacancies has been shown to occur at above 320 K and these vacancies have been shown to form clusters at ~ 380 K but at higher temperatures the clusters tend to break up making vacancy clustering more unlikely [5]. For both Mo and W the main bubble formation mechanism is thought to be vacancy clustering [47]. Some more general conditions are given to determine the likelihood of blistering. Chances of blistering are increased if the target material has a low solubility for hydrogen, if the sample is held at low temperatures, and if very high fluences of hydrogen ions are used. It was shown in section 2.2 that Mo (and W) has low solubility for hydrogen for low temperatures. In plasma experiments,

including tokamaks, ion fluence is typically very high making Mo and W PFCs prime candidates for blister formation.

Since many of the bubble formation mechanisms require a nucleation void to be in place before a significant bubble can form, one might expect an energy threshold for bubble formation. If the energy of the incident ion is too low to create vacancies then a lack of nucleation site may inhibit bubble formation. Some of the earliest work done on blister formation was performed by Verbeek and Eckstein [55]. They showed that room temperature exposures of Mo to 150 keV and 15 keV D⁺ ions created blisters whose size depended on material pre-treatment, such as annealing and cold-working. A critical fluence at which blisters are first observed was also defined. The critical fluence was found to be inversely proportional to incident flux, which is likely due to the fact that hydrogen is less mobile with higher implantation currents, so less time is given to the hydrogen to move out of the implantation zone [55]. With an ion energy of 15 keV there will be significant radiation damage induced in the sample.

Blister formation has been seen for deuterium ion energies as low as 67 eV [56]. The most complete study of low energy blistering effects in W and Mo was performed by Wang et al [57]. Tungsten samples were irradiated with deuterium ions ranging from 100-1000 eV across temperatures from 20-800 °C. Irradiation fluences ranged up to $1 \times 10^{25} D/m^2$ and some samples were pre-irradiated by 4 keV He⁺ ions. It was found that with increasing ion fluence, the number of blisters seen decreased but the size of each blister increased leading to an overall increase in voided volume with increasing fluence. A similar effect was seen by increasing the ion energy; higher ion energy corresponded to fewer but larger blisters seen on the surface. However it was also noticed, through IBA techniques, that the deuterium concentration near the implantation depth decreased with increasing fluence. This does not appear to correspond with blister formation at the implantation depth. Analysis of the top of a ruptured blister allowed them to determine the thickness of the lid, and thus estimate the depth at which blisters were being formed. The cover was estimated to be $\sim 0.5 \mu m$ thick, so the blisters are forming well past the implantation depth of 2-10 nm. Other studies have seen blister covers as thick as $\sim 10 \mu m$ [58]. For irradiations at higher temperatures, no blisters are observed but there is also $\geq 0.6 \mu m$ of material eroded from the surface

during the high-T 1 keV/D+ irradiations. It is not clear how the higher erosion yield effects blister formation. The pre-irradiations were shown to actually reduce blister formation but significantly increase overall retention. No blister formation was seen in Mo at 1 keV/D+ for RT and 800 °C irradiations. The erosion yield of Mo was ~ 3 times higher than that in W and this may be having an effect on blister formation [57].

Since the depth at which the blister formed was not well predicted by loop punching or vacancy clustering mechanisms, and the fact that there were large compressive stresses implied in the implantation layer, it was concluded that stress-driven blister formation was a more likely scenario than pressure-driven formation [57]. It is thought that blister formation is similar to two plates buckling under compressive forces. If enough imperfections (vacancies, damage sites) are available then stresses will concentrate at these imperfections and created a weakened interface region [59]. It has been shown that blistering at the interface relieves those stresses [59]. This theory is found to perfectly explain the relation of the blister cover thickness to the diameter of the blister [57].

There are some studies in the literature that conflict with observations by Wang et al. Others have seen a lack of blister formation at high temperatures in Mo [60] but a study by Sakamoto et al used transmission electron microscopy (TEM) to observe nanometer scale bubble for 500 eV H+ ion irradiation of Mo at 873 K [61]. However, blistering in Mo has been observed for low energy and low temperature irradiations. Thomas and Bauer observed blisters in Mo at fluences as low as 5×10^{22} D/m² with an incident flux of 1.25×10^{19} D/m²·s [60]. In a fusion experiment such as Alcator C-Mod, where the incident flux is $10^{20} - 10^{23}$ D/m²·s, a fluence of 5×10^{22} D/m² is obtained in 0.5-500 s. They also observed an order of magnitude drop in the number of blisters formed just by increasing the temperature from 0°C to ~ 100 °C. Sugie et al observed extensive blistering in Mo at ~ 100 °C [56]. Ion fluence was $0.4 - 1 \times 10^{25}$ D/m² with an incident flux of 5×10^{19} D/m²·s and the energy was 92 % D+ ions with the remainder of the ions (8 %) having energies of 100 or 200 eV. The samples were prepared by powder sintering and some of the samples used electron beam melting to create a smooth surface by covering up holes in the surface typically produced by powder sintering (the samples were meant to be mirrors). The samples with e-beam

melted surfaces experienced much worse blistering than the sintered and polished sample. E-beam melted surfaces showed blisters as large as $75\text{ }\mu\text{m}$ while the sintered and polished surface should blisters with diameters of $5\text{--}10\text{ }\mu\text{m}$. It was thought the elimination of the holes in the surface removed potential diffusion paths to the surface and thus decreased the resistance to blistering. For comparison, a W sample that was sintered and polished showed blisters an order of magnitude smaller in size. No explanation was given for this difference in size [56].

It is clear that, like most plasma-surface interactions, bubble and blister formation are complicated processes that depend on many variables. Both incident flux and fluence must be taken into account [55, 57] and ion energy also plays a strong role [57]. Also, surface preparation must be taken into consideration and sample annealing has also been shown to greatly reduce blister formation [62], most likely by removing inherent vacancies and voids produced by sample production (cold working, sintering, etc.). An elevated surface temperature can also prevent surface blistering and this may be similar to why annealing can help prevent blistering. Another interesting behavior has been observed when a continuous layer of Mo_2C is formed on the surface (as might occur in the divertor of a multi-material device such as ITER), that irradiation with D^+ ions will lead to blistering [63]. It is thought the carbide layer hinders the release of D, which eventually brings about surface deformation. So, it appears surface impurities must also be taken into account. It is important that the mechanisms for blister formation be well understood since blisters and bubbles are essentially unsaturable traps. Blister formation in the walls of a tokamak could lead to unacceptably high fuel retention, even in materials with supposedly favorable retention properties.

Several factors that could explain the large retention rates observed in Alcator C-Mod are found in the literature. Certainly the fact that a saturation fluence for Mo has not been found is worrisome. Also the evidence of blister formation for low-E but high flux and fluence D^+ ion exposures could be part of the explanation. However, in a system such as Alcator C-Mod where different locations experience different temperatures, fluxes, fluences and energies and PFC are produced using several different techniques and materials (Mo, TZM, Mo with boron coatings, upset forged,

hot-rolled, etc.) there are still numerous possible causes for this apparent high retention rate. However in general the high retention rates are generally regarded as surprising and worrying to the fusion research community.

2.4 Irradiation of Mo

While determining the quantity and location of trap sites is of great importance, for dynamic studies the source and production of the trap sites must also be determined and quantified. Trap sites are imperfections in the lattice of the substrate, most commonly single vacancy sites (see section 2.3) but these can also include vacancy clusters, dislocation loops, or voids. To create trap sites, the surface must be perturbed and damaged. One clear source of this damage is the impact and implantation of high-energy particles into the surface region, known as irradiation.

Typically in a fusion experiment, the plasma ions do not have high enough energy to form vacancies in the surface. Simulations in the SRIM program show that the threshold energy of deuterium ions to form vacancies in a Mo substrate is 300 eV. However in a DT fusion reactor, high-energy particles, including 14 MeV neutrons and 3.5 MeV alphas from DT burn, energetic ions from neutral beam charge exchange, and 3 MeV neutrons from DD burn, are capable of irradiating Mo. The alpha particles are predicted to lose most of their energy before they escape the core (alpha heating) although some fraction of alphas may be promptly lost to the wall due to plasma instabilities, or in the case of stellarators in particular unconfined fast particle orbits. Another source of fast ions is plasma heating. Prompt ripple loss of energetic ions (0.1-1 MeV) formed after ionization of neutral beams is one example. A particular concern for Alcator C-Mod is the production of fast ions by Ion Cyclotron Radio Frequency heating, the principal auxiliary heating method in C-Mod. Recent studies [64] have shown that the formation of high energy sheaths by RF sheath rectification leads to very high erosion rates of B and Mo at surfaces connected by field lines to the ICRF antennae, and is now thought to be the principal reason for elevated core Mo in H-modes. The sheath voltage of 500 V provides high energy implantation of deuterium (500 eV) as well as for the boron ions (singly-triple charged, 500 - 1500 eV). While this occurs over a relatively small area of the wall near the divertor, it appears to be an effect which dominates impurity production,

and therefore, one may presume, be an important effect with regards to producing surface defects through irradiation. We further note that ICRF is one of the principal heating schemes planned for ITER, and its field lines are connected to the portion of the divertor armored with tungsten. The 14 MeV neutrons, because of their lack of charge, cross electromagnetic fields and will reach the PFC with no energy loss. As the neutron passes through the PFC it will displace Mo atoms from their lattice points due to elastic collisions with the material nuclei, and these displacements may result in vacancy trap sites. Unlike the ions which cause damage at PFC surfaces, the neutrons will cause displacements uniformly throughout the bulk of the PFC since their stopping distance is on the order of meters. Because of the presence of both high energy neutrons and high-energy alphas, it is important to understand the irradiation characteristics of Mo bombarded by these particles. For reference, it is expected that PFC will receive 20 dpa per operational year in a fusion reactor, highlighting the requirement for understanding the response of fusion materials to displacement damage. The typical DD burn neutron production rate is modest ($\sim 10^{13}$ - 10^{14} n/s) in Alcator C-Mod due to its lack of heating neutral beams. This range of neutron flux dispersed over the ~ 10 m² wall in Alcator C-Mod, does not provide substantial displacements in the PFC.

Neutron irradiation can affect hydrogenic retention properties in many ways. The displacements caused by the irradiation can lead to the production trap sites which can lead to an increase in overall hydrogen retention. Neutron irradiation of Mo can also lead to a reduction of diffusivity and permeability of H in Mo as was shown by Katsuta et al. [10]. For their experiments, a high-purity (99.99 %) poly-crystalline Mo specimen was subjected to non-thermal ($E_n > 1$ MeV) neutrons to a total fluence of 3.0×10^{15} and 1.2×10^{17} n/cm² at an irradiation temperature of $< 300^\circ\text{C}$. The neutron irradiation corresponded to damages of 10^{-5} - 10^{-3} displacements per atom (dpa). The time-lag method [33] to determine the diffusivity in irradiated and un-irradiated Mo was used. The results showed the diffusivity was reduced by 10% and 20% from the diffusivity in un-irradiated Mo for neutron fluences of 3.0×10^{15} and 1.2×10^{17} n/cm² respectively. The activation energies for diffusion were not drastically changed by the n-irradiation. The activation energies were 0.15 eV and 0.17 eV for neutron fluences of 3.0×10^{15} and 1.2×10^{17} n/cm² respectively as compared to 0.16 eV for the un-irradiated Mo in this experiment. These activation energies are

similar to the result of 0.11 eV from previous work on un-irradiated Mo (see section 2.2 and [33]). It was suggested, from X-ray diffraction, that the hydrogen was being trapped by dislocations and that hydrogen that was bound to mobile dislocations can diffuse at a *higher* rate than the normal lattice diffusion rate [10, 65].

Nielsen et al have demonstrated the growth of voids in Mo by neutron irradiation and then annealing at elevated temperatures [66]. High-purity Mo was irradiated by fast neutrons to a fluence of 1.72×10^{18} n/cm² and then annealed to 450°C or 650°C in vacuum to stabilize the neutron-induced defects into voids. The positron annihilation technique [67] was used to monitor the trapped hydrogen and empty voids as the Mo sample is heated. This technique showed that electrolytically injected hydrogen traps in the voids in two states. The first state was the hydrogen recombining inside the void and becoming trapped as H₂ with a trap energy of 0.5 eV. The second state was H that is chemisorbed to the surface of the void with a trap energy of 1.3 eV. The trap energies were in agreement with predicted values based on other experimental results. It is important to remember that the neutron irradiation itself does not form the voids in the Mo. Heat treatment was needed after irradiation to form stable voids from the monovacancies and dislocations caused by the irradiation.

For the purposes of hydrogen retention, it is important to be able to predict what types of lattice defects will be produced by fast neutron irradiation. The type of trap available to the hydrogen can affect the trap energy and also how many H can be trapped in a single defect. Hyodo et al used the positron annihilation technique to identify what lattice defects are formed in single crystal Mo at 100°C that is irradiated by fast neutrons to a fluence of 6.5×10^{19} n/cm² [67]. Results indicate that the neutron irradiation resulted in the formation of small defects, such as monovacancies, divacancies, and dislocation loops, and larger vacancy clusters of the average size of approximately 12 vacancies. These defects were created in approximately equal parts (55% small defects and 45% vacancy clusters) and there was no evidence of intermediate-sized vacancy clusters. The clustering of vacancies at intermediate temperatures is in agreement with the work of Condon et al [5] (see section 2.3).

Because fast neutron sources are rare and typically have very low fluxes, high energy protons are often used to simulate neutron damage. This was the case in a series of papers by Oliver et al. [68, 69] where 800 MeV protons were used to irradiate 0.25 mm thick poly-crystalline W samples. Irradiations of 0.31 dpa and 7.9 dpa were performed at temperatures of 300-400 K. Proton irradiation not only produces lattice damage in the target but it also results in a H inventory in the target. In the first paper [68], TDS was performed on the irradiated W samples and an un-irradiated control sample to determine the H inventory from irradiation and how the H was trapped. TDS results show two main desorption peaks. One peak is located at a desorption temperature of ~ 550 K. This desorption peak is actually thought to be surface defects introduced during material fabrication or sample cutting and preparation. The second peak is located at ~ 1400 K, a very high desorption temperature for H trapped in W. The 1400 K desorption peak was much greater for the 7.9 dpa case than the 0.31 dpa case and the total H inventories were 448 appm and 1990 appm for 0.31 dpa and 7.9 dpa respectively. Modeling these results with TMAP4 resulted in best fits if a trap density of 4-7% was assumed throughout the entire depth of the sample. The total inventories of the two dpa-cases was matched by adjusting the fraction of traps that were filled. These trap densities are higher than any previous experimental hydrogenic retention results for W indicating that the majority of these traps are produced by the irradiation. It is also interesting to note that the best fit trap densities were the same for both dpa-cases indicating a trap density saturation. Since trap densities of this magnitude would be unacceptable for hydrogenic retention in a fusion reactor, a follow-up experiment was performed where irradiated samples were exposed to a deuterium DC glow discharge after annealing [69]. Tungsten samples that had undergone the same irradiation conditions were annealed at 1273 K for 6 hours to remove the H inventory from the irradiation. These samples plus an un-irradiated control sample were then exposed to a deuterium DC glow discharge for 6 h for a D fluence of $\sim 2.5 \times 10^{20}$ D/cm² and ion energy of <100 eV. These samples were then thermally desorbed in the same manner as the previous experiment [68] but with much different results. The TDS results for the un-irradiated and irradiated samples were very similar. All spectra showed peaks at ~ 550 K and ~ 800 K. Modeling with TMAP shows these peaks to be best fit by a trap density of 20% over the first 30 nm, the implantation region, and a trap density

of 2 appm distributed over the entire thickness of the sample. The only difference between the un-irradiated and irradiated spectra is the addition of a peak at ~ 400 K for the irradiated samples. This peak is thought to be caused by oxide related traps that were caused from the submersion of the sample in water at ~ 440 K during the irradiation. Obviously the high trap densities that were seen after irradiation were no longer present. This indicates the ability to anneal out virtually all irradiation damage in W and may indicate a fusion reactor operating at high wall temperatures may not be as strongly effected by radiation effects. However in present devices, and in ITER which uses water cooling for PFCs, the maximum temperature wall temperature is well short of the annealing temperatures (>1200 K) used in these studies.

Takagi et al have examined the retention of deuterium in Mo irradiated by 0.8 MeV ^3He [49]. In this study a 100 μm thick Mo foil separated two vacuum chambers. This allowed for permeation measurements to determine the diffusion rate of the Mo and for nuclear reaction analysis to be performed with a 1.7 MeV ^3He ion beam. The upstream side of the Mo foil was exposed to a deuterium RF plasma, once the permeation flux through the downstream side reached steady-state, the foil was irradiated with 0.8 MeV ^3He ions. After the exposure, the surface was analyzed with nuclear reaction analysis. From the permeation study a diffusion activation energy of 0.55 eV was found for temperatures between 452-568 K. The nuclear reaction analysis of the foil surface showed a depth profile with a broad peak at ~ 0.8 μm initially. As the 0.8 MeV ^3He irradiation fluence increased, this peak shifted to a depth of ~ 1 μm . These depths are similar to the peak of the damage distribution of 0.8 MeV ^3He ions in Mo. However, there was also significant retention in the near-surface (<0.4 μm) region where there would be virtually no damage from irradiation. This indicated the migration of traps from the damage zone back towards the surface. There was also retention seen at depth greater than the range of 0.8 MeV ^3He in Mo, again indicating the migration of trap sites. A trap energy for these radiation produced trap sites was found to be 1.1 eV by relating the trapped deuterium (measured with the nuclear reaction analysis) to the amount of deuterium in solution (inferred from the permeation measurements) for temperatures ranging from 530-603 K. The concentration of trapped deuterium was also measured as a function of irradiation fluence. The trapped deuterium concentration increased with every increase in irradiation fluence

showing no signs of saturating. The maximum irradiation fluence was $1.5 \times 10^{21} \text{ }^3\text{He/m}^2$. Higher fluences could not be examined since they could cause more macroscopic damage to the surface such as blistering. The maximum trap density measured was $2 \times 10^{27} \text{ traps/m}^3$ or $\sim 3 \text{ at.}\%$. The dependence of trap density on irradiation fluence also can yield a conversion factor for the creation of trap sites from displacements per atom. In this case a linear dependence was assumed with a conversion factor of 0.007. It is interesting to note that Takagi et al saw no saturation in terms of trap density versus dpa while the model from Oliver et al [68, 69] showed no change in trap density from 0.31 dpa to 7.9 dpa. It is important to note the work by Takagi was performed on Mo while the work by Oliver was performed on W and this may indicate a key difference between these two similar metals.

Ibragimov et al examined the damage caused by proton-irradiation of Mo [70]. Annealed Mo foils were irradiated by 6-30 MeV protons for fluences of $5 \times 10^{19} - 5 \times 10^{22} \text{ m}^{-2}$ at room temperature. Transmission electron microscopy (TEM) was used to characterize the damage in the Mo foils as a function of proton fluence and energy. The types of traps produced were vacancy clusters with a mean diameter of $\sim 1.7 \text{ nm}$. This did not change with proton energy or fluence although the number of clusters seen did increase with proton fluence. From modeling, there are strong indications that there are a large number of defects present in the Mo that are too small for the TEM to resolve.

Because high-energy alphas are present in a fusion reactor and for reasons that will become more apparent in section 3.2, it is also important to understand how alpha-irradiation may affect the hydrogenic retention properties of Mo. Ibragimov et al also examined the damage caused by alpha-irradiation of Mo [70]. Mo foils were irradiated by 10-50 MeV alphas to fluences of $5 \times 10^{18} - 2 \times 10^{21} \text{ m}^{-2}$. The type of defect produced was similar to the proton irradiation case however the vacancy clusters were closer to 3 nm in size. The amount of damage induced by the alpha irradiation was approximately twice that of the proton irradiation. Another key difference is the stopping power of Mo for alphas is much greater than that for protons. This allows the alphas to backscatter into the path of damage more easily. This can result in the vacancies produced being occupied by the implanted He rather than remaining empty for a potential H trap. It is also

clear from comparisons of the experimental data to the theoretical prediction of damage, that the formation of a large number of interstitial defects, as is the case for alpha irradiation, can lead to enhanced recombination with available vacancies. It follows that the trap production will not scale linearly with displacements per atom. With 14 MeV neutron bombardment, (n,α) reactions will also produce bulk helium that could fill available trap sites.

Naidu et al investigated the behavior of damage sites in Mo caused by alpha irradiation using the positron annihilation technique [71]. Poly-crystalline Mo samples were irradiated with 30 MeV alphas to a fluence of $1.2 \times 10^{17} \alpha/\text{cm}^2$ at a temperature <420 K. After the irradiation, positron lifetimes were monitored during an annealing to 1500 K. The results indicate the formation of vacancies and dislocation loops from the initial irradiation. As the annealing temperature reached 420-570 K, the results indicate that the vacancies became mobile and began to cluster into vacancy clusters. At the annealing temperature of 920 K, the clusters began to coarsen into voids. At this temperature, dislocation loops start dissociating and annealing out as well. It is not until temperatures in the range of >1220 K, do the voids begin to anneal out. It is important to acknowledge that trap sites are mobile and in some cases can be more mobile than interstitial hydrogenic species.

Shinno et al have investigated the effects of alpha irradiation of intermediate energy ($E_\alpha = 50\text{-}150$ keV) over a wide range of temperatures (413 - 1298 K) and for fluences in the range of $10^{22}\text{-}10^{23} \alpha/\text{m}^2$ [72]. The effects on structure were observed with SEM images. The results showed extensive blistering and flaking of the Mo surface under alpha irradiation. With increasing fluence, the blistering and flaking increases in areal density and depth into the surface. At these intermediate energies it is expected that the surface would show the majority of the damage since the implantation range for 100 keV alphas into Mo is only ~ 250 nm. As the irradiation temperature increases the flaking begins to decrease but the blistering is still present. At 923 K, flaking no longer appears but blisters with diameters of $\sim 10 \mu\text{m}$ are still present. At 1098 K the surface becomes porous and blisters are reduced greatly in size a diameter of ~ 200 nm. Surface flaking, erosion, and damage showed no sign of saturating with incident alpha fluence. In terms of PFC performance in a reactor environment, flaking can be very detrimental as it introduces large

amounts of wall material into the edge plasma. This can lead to unacceptably high energy losses in the plasma or disruptions. Dust and flake formation can also lead to serious safety concerns if these flakes have significant amounts of tritium trapped in them.

Hino et al examined the effects of low energy (<10 keV) alpha irradiation of Mo and its effect on hydrogenic retention. The Mo samples were exposed to 5 keV alphas to a fluence of $1.4 \times 10^{18} \alpha/\text{cm}^2$ and then exposed to a hydrogen ion beam. The hydrogenic trapping was investigated using TDS and the results were compared to Mo samples that were exposed to the H ion beam without prior exposure to the alpha irradiation. It was found for the un-irradiated Mo sample, there were two major desorption peaks, at 200°C and 400°C . For the alpha irradiated sample, the total amount of trapped H remained the same but the majority of the H was found in the 200°C peak and the 400°C peak was reduced to almost zero. It is thought that the increase in the 200°C peak corresponds to increased defects near the surface caused by the alpha irradiation. At such low energies and low temperature it is expected that the irradiation effects would be isolated to the surface of the Mo. A Mo sample was also irradiated when it had been pre-implanted with hydrogen. It was found that the alpha irradiation actually reduced the trapped hydrogen in the sample. This effect appeared to be saturated at a 50% reduction of the pre-irradiation hydrogen inventory.

The effects of alpha irradiation can vary dramatically with energy. High-energy (>1 MeV) alpha irradiation can form mobile vacancies and vacancy clusters to the end of range [70, 71]. While intermediate energy ($10 \text{ keV} < E_\alpha < 1 \text{ MeV}$) alpha irradiation is more likely to form larger voids and surface blistering, especially at elevated temperatures [73, 74, 72]. Low energy ($E_\alpha < 10$ keV) alpha irradiation can actually desorb H from a surface and change the trap mechanism for trapped H [75]. Neutron irradiation has shown that it can drastically change both the trap densities [68, 69] and hydrogenic transport [10].

Chapter 3

Experiment and Materials

3.1 The DIONISOS Experiment

The Dynamics of ION Implantation and Sputtering of Surfaces (DIONISOS) experiment was designed to fill the strong need for an experiment to study the dynamics of plasma-surface interactions (PSI). Easily implemented plasma diagnostics in a tokamak, such as optical emission spectroscopy (OES), cannot measure *net* surface effects on a PFC. PSI studies in tokamaks have typically relied on "post-mortem" techniques. A surface is examined before being installed into the tokamak, exposed to a range of one discharge to many years of tokamak operation, and then removed for re-examination. This allows for the measurement of net effects averaged over its duration in the tokamak, but this method completely ignores the dynamics of the PSI, which makes it very difficult to extrapolate current PSI results to future long-pulse or steady-state devices. Currently the only real-time PSI diagnostic is a quartz micro-balance (QMB). QMB measure the net erosion/deposition process by measuring changes in the quartz crystal resonant frequency which varies with the deposited/eroded surface mass. However, QMB are limited in their usefulness since they have no elemental discrimination of the film deposited on its surface. QMB are also very sensitive to temperature, so they typically must be removed from direct plasma contact, making it impossible to use them for most divertor PFC studies.

The DIONISOS experiment allows real-time, in-situ IBA measurements of a material surface before, during, and after a plasma exposure (Fig. 3.1). This ability to examine how the surface changes upon initial plasma contact and how the surface evolves over prolonged plasma exposure and after the plasma source is removed is invaluable for studying the dynamics of PSI and still

Figure 3.1 A schematic of the principle of operation for DIONISOS.

Figure 3.2 The DIONISOS experiment

Figure 3.3 A 3-D representation of the DIONISOS vacuum vessel

allows for DIONISOS measurements to be compared to other “post-mortem” results. *The design, fabrication and commissioning of the unique DIONISOS facility forms a major portion of the research work carried out for this thesis.*

3.1.1 DIONISOS Facility

In figure 3.2 much of the structure of DIONISOS can be seen to be helmholtz magnets, cooling lines, power supplies and lines and support structure, but from an experimental point of view the vacuum vessel and the sample holder are the two most important components.

The main purpose of the DIONISOS vacuum vessel was to allow the greatest amount of diagnostic and physical access, while minimizing the size. The custom-built vessel has 19 diagnostic ports, 5 of those being line-of-sight ports onto the sample surface (see Fig. 3.3). A hinged door on the back of the vessel allows for easy access to the interior and the sample holder for sample changing or maintenance. Vacuum of $\sim 10^{-8}$ torr has been achieved, although typical vacuum tends to be closer to $1 - 2 \times 10^{-7}$ torr.

The DIONISOS sample holder is required to create a large number of surface conditions while maintaining the flexibility to be able to hold a large variety of sample shapes and sizes provided there is a flat surface to allow good mechanical and thermal contact to the heat sink. The sample holder consists of a copper plate heat sink suspended in the vessel from above. It is mounted on a rotatable platform (see Fig. 3.2). This allows for a full 360° of rotation and control over the incident angles of the ion beam or plasma (although the angle between the plasma and ion beam is fixed at $\sim 45^\circ$). This control is very important since IBA techniques are extremely sensitive to geometry and it also allows the recreation of grazing incidence magnetic field lines such as those seen on a tokamak main wall. The heat sink has both water and air cooling capabilities and can also be actively heated by cartridge heaters clamped to the back of the plate. The active cooling and heating of the sample provides very stable temperature control ranging from 300-750 K using a feedback control with thermocouples or resistive temperature devices (RTD). Surface temperature is of critical importance when dealing with PSI as was shown in section 1.2.

The heat sink is electrically floating with respect to the chamber walls, which allows the sample to be actively biased. The sample bias controls the energy of the incident plasma ions, which is critical for sputtering or implantation studies. The sample is biased through a stainless steel (SS) support rod. The support flange and cooling lines are isolated from the chamber with ceramic breaks, the power leads for heating are isolated with ceramic stand-offs on the back of the plate (the heaters themselves are incased in ceramic and a floating SS sheath), and the thermocouples and RTD are all ungrounded (see Fig. 3.4).

Sample bias can range from the plasma floating potential to 600 V. The sample plate is 10 cm x 9 cm and the ion beam can scan across the entire surface of the plate. A glass plate is attached to the back of the sample holder for beam alignment and calibrations (see Fig. 3.5). The entire sample plate can be completely removed for maintenance or replacement with another custom heat sink for samples of inconvenient shapes (rods, spheres, etc.) or sizes (excessively thick samples).

Table 3.1 summarizes the range of surface conditions achievable with the DIONISOS sample holder.

Figure 3.4 The DIONISOS sample holder.

3.1.2 Helicon Plasma Source

The plasma source for the DIONISOS experiment is an RF helicon plasma source. A helicon mode source provides exceptionally high density and low temperature plasmas, which is important for recreating the high ion fluxes and fluences found in a tokamak environment. The source consists of an $m=1$ Nagoya type III antenna surrounding a cylindrical quartz tube. The antenna is attached to a 5 kW RF power supply through a manual match network. Typical plasmas experience $< 5\%$ reflected power. The plasma parameters are measured in real-time by a scanning Langmuir probe. Plasma density and temperature have been measured across the plasma column (see Fig. 3.7).

The plasma flux, and hence the density, can be seen to decrease as the radial position from the center increases. This peaked profile has been confirmed by IR thermography of the plasma spot. This dependence of flux density on radial position provides the ability to measure the effect of various plasma fluxes by simply analyzing different points of plasma contact within the column. The ability to resolve the evolution of PFC surfaces in time, depth and lateral location on the

Figure 3.5 A view of the sample holder inside the vacuum vessel a) without plasma and b) with plasma.

Surface Parameter	Range of values for DIONISOS sample holder
Magnetic field	≤ 0.9 kG
Angle of incidence	$0^\circ - \pm 90^\circ$
Surface Temperature	300 – 750 K
Sample Bias	$eV_{float} - 600$ V
Plate width	~ 10 cm
Plasma diameter	~ 5 cm
Ion beam spot diameter	~ 0.2 cm

Table 3.1 Surface conditions available to the DIONISOS sample holder.

surface within a single experiment is a unique strength of DIONISOS. In this study the center of the plasma column was used as the analysis point for the majority of experiments. Plasma density and flux are also strongly related to the magnetic field and the amount of RF power into the plasma (see Fig. 3.8). Although our power supply is rated up to 5 kW of RF power, operations are limited to ~ 2 kW of RF power due to limited cooling on the RF antenna and helicon flanges.

The quartz tube and DIONISOS vessel is surrounded by a set of four helmholtz coils. Up to 300 A of current is passed through the helmholtz set to generate a magnetic field of up to ~ 0.9

Figure 3.6 The DIONISOS helicon plasma source creating a deuterium plasma.

kG. The plasma is collimated by the magnetic field and extracted from the source by either plasma pressure in the case of no sample bias, or by the active bias onto the sample. The collimated plasma impacting the sample can be seen in Fig. 3.5. Neutral gas is fed into the back of the quartz tube and gas flow is controlled by a mass flow controller or a manual needle valve. Neutral gas pressure inside the vacuum vessel is measured by a capacitance manometer during plasma operations. Differential pumping along the beamline allows neutral pressures to be as high as 10 mtorr, however optimal neutral pressures for deuterium plasmas were found to be 4.5 – 6 mtorr.

3.2 DIONISOS Diagnostics

The primary diagnostic of the DIONISOS experiment is a 1.7 MV Pelletron tandem ion accelerator. The ion accelerator provides ions with energies of ≤ 10 MeV, which are required to perform IBA of surfaces. The accelerator has two different ion sources that can either provide very high ion beam currents (100's μA) for relatively short amount of time (≤ 20 hours) or much lower beam currents (≤ 4 μA) for virtually indefinite steady-state operation. The available beam species are only limited by an atom's ability to form negative ions, but almost all elements can be formed into an ion beam with the Pelletron accelerator. The most common beam species are H, ^4He , ^3He , and O. Beam focus and steering are also very controlled in the ion beam. Beams can be focused on

Figure 3.7 The flux density and electron temperature as a function of column radius for the helicon supply. Measurements were taken for a deuterium plasma with $B = 500 \text{ G}$ and $P_{RF} = 500 \text{ W}$.

the target using a post-accelerator quadrupole magnet. Magnets and electrostatic steerer plates are also used to move the beam spot both horizontally and vertically across a sample. DIONISOS has no limiting apertures so that all locations on the target are accessible to the ion beam. Horizontal and vertical control of a very tight beam spot ($\sim 2 \text{ mm}$ or $1/10$ of the plasma diameter) allows for detailed scans of PFC surfaces to be made.

IBA bombards a surface with ions of a single species with a single, known energy. Energetic particles, and in some cases gamma rays, are then emitted from the surface either due to nuclear scattering processes or nuclear reactions. The energetic particles can be detected with a solid-state detector that records the energy of each detected particle. The signals from the detector are read into a multi-channel analyzer and an energy spectrum of detected particles is produced.

Figure 3.8 a) The plasma flux and density as a function of magnetic field for an argon plasma, and b) the plasma flux as a function of RF power for a deuterium plasma in the DIONISOS helicon supply. These values are averaged over the entire column.

Since the energy-resolved cross-sections and kinematics for all the processes involved are well-known, simulation programs can be used to re-create the energy spectrum and reveal the depth-resolved composition of the surface. IBA consists of three main techniques of analysis: nuclear reactions analysis (NRA), Rutherford backscattering (RBS), and elastic recoil detection (ERD). An interesting question is whether or not IBA is possible during a plasma exposure. If IBA detects energetic particles then wouldn't particles sputtered from the surface create noise in the signals? Do the beam ions interact with the plasma ions? How does the magnetic field affect ion beam focus and steering? It turns out that these questions are all non-issues since there is such a large energy gap between beam ions and plasma ions. While beam ions are in the MeV-range, the plasma ions are in the eV-range. The mean free path for a beam ion in an eV-scale plasma is on the order of

meters, so there should be little to no interaction as the beam ions enter a 2 cm diameter plasma. However, particles sputtered off the sample surface will also be in the eV-range and will have a mean free path on the order of millimeters, so there is a good chance the sputtered particle will be ionized and re-deposited before escaping the plasma column (very similar to what happens in a tokamak). The magnetic field is an issue in the respect that it does deflect the ion beam, however, since the beam can be visually aligned, any deflection (typically ≤ 1 cm for most ion beam and magnetic field combinations) can be compensated for with the electrostatic steering plates for the ion beam. This exploitation of the energy gap between plasma particles and beam ions makes the DIONISOS concept possible.

NRA uses energetic beam ions to induce nuclear reactions between the ion beam species and a particular element in the PFC. The reaction usually results in the creation of a daughter atom and an energetic proton or alpha particle. The proton or alpha can then be detected with a solid-state detector (see Fig. 3.9a). Nuclear reactions that result in gamma emission can also be used if a gamma detector is available, and this process is referred to as Particle-Induce Gamma Emission (PIGE). One advantage of NRA is that nuclear reactions have energy-dependent cross-sections which can result in narrow energy resonances for the reaction. By controlling the ion beam energy accurately, these narrow energy resonances can be exploited to yield very high depth resolutions ($\sim nm$) even microns deep in the PFC. NRA is also unaffected by the mass of the target nucleus and is isotope dependent. This allows for easy differentiation of isotopes that are very close in mass and difficult to distinguish from each other by other means. The isotope sensitivity is very important for these PSI studies since it allows for hydrogen and deuterium to be detected independently of one another. Some disadvantages of NRA are that reaction cross-sections are typically small, making it difficult to obtain good counting statistics, some of the energetic products are so energetic that special high depletion depth detectors or very thick absorbing foils are required. Also, NRA can typically only measure one component of the surface at a time, although an ion beam of ^3He has nuclear reactions with D, B, O, and C all of which are commonly found on PFC surfaces. However this can also result in overlapping energy peaks making analysis and interpretation difficult. An example of a fitted NRA spectrum can be seen in Fig. 3.10a.

Figure 3.9 Schematics demonstrating the principles of a)NRA, b) RBS, and c) ERD.

Figure 3.10 Examples of fitted spectra for a) NRA, b) RBS, and c) ERD. The x-axis is the channel number, which typically corresponds linearly to particle energy. The y-axis is the number of detected particles in each energy channel. The solid lines are fits to the experimental data using the sim-NRA numerical simulation code.

RBS is the detection of beam ions that are backscattered off the PFC surface. To maximize the kinematics and detection depth of this technique, light (low-Z) beam ions, usually proton or alpha beams, are used to detect heavy (high-Z) atoms. The backscattered beam ions are detected and an energy spectrum is created (see Fig. 3.9b). RBS has the advantage of strong cross-sections so statistics for the energy spectrum are good. However, the disadvantage of RBS is that it is very difficult to detect small amounts of lighter elements in a high-Z medium since the Rutherford cross-section is proportional to Z^2 . This is critical for PSI studies of Mo or W since the signals from the high-Z lattice will dominate the spectra. Elements such as carbon or oxygen cannot be measured directly since the signal for a small amount of C or O does not significantly affect the strong background signal from the Mo or W. The amount of oxygen or carbon on the surface can still be deduced by observing how much Mo is *missing* on the surface rather than trying to observe the C or O peaks directly. In some cases, the incident ion can overcome the coulomb repulsion resulting in a “non-Rutherford” scattering cross-section that is much higher than the classical Rutherford cross-section. For example, this enhanced cross-section allows B to be seen with Mo background using proton RBS (see Fig. 3.10b).

ERD is the detection of energetic particles that are elastically forward-scattered by the beam ions. To create a forward scattering event, the ion beam must be at a grazing angle to the surface and the beam ions must be heavier than the surface particle that is to be detected (see Fig. 3.9c). Thin foils are used to shield the detector from beam ions that are reflected off the surface of the sample. The ability of ERD to detect light particles makes it ideal for detecting hydrogen and deuterium in the near surface. In fact, one advantage is that ERD spectra can easily distinguish and simultaneously measure H and D signals. Another advantage to ERD is that there is no signal from a high Z material (provided the beam ions are light enough) so there is no background signal in the spectra. However, because a grazing angle of incidence is required, the detection depth of ERD is limited. This technique is also very sensitive to the scattering geometry, with a half-degree change in scattering angle making a large difference in the spectra. This can make re-creating the spectra with a simulation program difficult if there is some uncertainty on the geometry of the experiment (see Fig. 3.10c).

Figure 3.11 The reaction cross-section for the $^3\text{He}(d,p)\alpha$ nuclear reaction as a function of ^3He ion energy.

For hydrogenic retention studies in Mo, the NRA technique is used. The nuclear reaction used for deuterium reaction is $^3\text{He}(d,p)\alpha$ where the proton and alpha have various energies depending on the geometry, following from momentum and energy conservation with the $Q=18.3$ MeV nuclear reaction. For the geometry found in DIONISOS, $E_p \approx 15.4$ MeV and $E_\alpha \approx 2.4$ MeV. The cross-section for this reaction is fairly constant for $E > 1500$ keV, but below 1500 keV, the cross-section peaks at ~ 700 keV before rapidly decreasing as the energy goes to zero (see Fig. 3.11). Either the proton or the alpha can be detected depending on the thickness of the absorbing foil in front of the detector. It is easier to detect the alpha if you are examining very near surface concentrations since alphas do not have a long range in Mo. Protons, having much higher initial energy and lower stopping rates, can be easily detected even from the maximum range of the ion beam in Mo. The energy for the ^3He ion beam used for analysis in this study is ~ 3.5 MeV, which, when combined with an incident angle of 45° , corresponds to a maximum measurement depth of $\sim 5 \mu\text{m}$. This represents Mo well into the "bulk" material for plasma exposures, where typical plasma ion implantation depths are < 10 nm.

Figure 3.12 The Gaussian peaks produced by simNRA from a series of discrete, 1 μm layers with a concentration of 0.01 D/Mo.

The simulation program that is used in this study to re-create experiment spectra is simNRA [76, 77]. This simulation program allows the user to create a target of discrete layers of varying elemental composition and will create a predicted experimental spectrum that will be produced by that target. The discrete layers in the simulation program produce discrete Gaussian peaks at known energies (based on the depth in the target). The height of the Gaussians are determined by the D/Mo ratio in they corresponding layer in combination with the reaction cross-section for those energies, and the width of the Gaussians is determined by the thickness of the layer (with a lower limit to the thickness being set by the depth resolution of the experiment). The Gaussians are then summed together to produce the simulated energy spectrum. Fig. 3.12 shows the Gaussians produced by discrete 1 μm thick layers at a concentration of 0.01 D/Mo, down to a depth of 6 μm in the surface. The differences in the magnitudes of the peaks is due to the energy dependence of the reaction cross-section (see Fig. 3.11). The fact that the layer from 5-6 μm yields no Gaussian is proof of the 5 μm detection limit for the 3.5 MeV ^3He NRA. In order for the simNRA program to be accurate, the experimental parameters must also be well known. These parameters include ion beam species and energy and the geometry of the experiment including incident angle of the ion

beam and the scattering angle associated with the solid state detector and the solid angle covered by the detector. Since the positioning of the detector is fixed in DIONISOS and the orientation of the target is well controlled, the geometry of the system is well-known. The energy calibration of the detector and the thickness of any foils placed in front of the detector are also required. Detector energy calibrations can be made if spectra have multiple peaks. The $C(^3\text{He},p)N$ nuclear reaction is used for energy calibration since this reaction yields protons of 3 different energies, and these three peaks are used to calibrate the detectors. For $^3\text{He}(d,p)\alpha$ NRA, because the proton produced has such high energy, ~ 15 MeV for this geometry, a 1 mm Al foil is needed to slow down these protons enough to be fully stopped in the detector (500 μm depletion depth). Unfortunately, using a foil this thick limits the depth resolution of the experiment due to a broadening of the energy distribution by straggling of the detected protons. The limit of the depth resolution for this experimental set-up is ~ 250 nm for D in Mo. By creating a layer structure that re-creates the experimental spectrum, it can be inferred that the chemical composition of the layer structure closely resemble the chemical composition of the target surface, both in depth distribution and total concentration. This technique can measure D concentrations as low as 10's of appm (i.e. 0.00001 D/Mo)..

Typically, ion beam analysis is thought of as a non-perturbing diagnostic. In a static environment, when the surface is in equilibrium, this is true. However, in a dynamic environment, such as in DIONISOS, ion beam analysis is not only a diagnostic but also a trap production mechanism. This can be considered either a disadvantage or an advantage. As a disadvantage, one generally does not want a diagnostic probe to be too perturbing. As an advantage the high energy ion beam can reproduce the conditions of a burning fusion reactor where high-energy particles will be impacting the walls simultaneously with the plasma ions. Recall that it has already been shown that irradiation of Mo can also increase the hydrogenic retention properties (See section 2.4). Despite the ion beam covering a much smaller area than the plasma, the trap production from the ^3He irradiation of the surface must be taken into account since it is the same ^3He ions that are detecting the trapped deuterium. The relative amount of damage is controlled externally by the user by varying beam current and spot size. One experimental limitation to reducing the beam current is the requirement for diagnosis of sufficient counts for measurement accuracy. Increasing the

Figure 3.13 Comparison of the dpa distribution as a function of depth and ion range of 3.5 MeV $^3\text{He}^{++}$ in Mo at an incident angle of 45° as obtained by TRIM. The ion beam current density for this damage profile is 0.087 A/m^2 , a typical current density for NRA measurements in DIONISOS.

spot size also decreases damage in relation to the plasma, but reduces spatial resolution. We note that these limitations can be also externally controlled by having detectors with sufficiently active cooling that the solid angle of the detector to the beam-material interaction spot can be arbitrarily increased to improve counting rates. Although we have not implemented this feature for these experiments, in general we conclude that the ability to both diagnose and damage the surface in a controlled manner is on the whole an advantage.

It is reasonable to assume that trap production is related to displacements per atom. TRIM simulations for alpha irradiation of Mo show that the majority of the displacements occur near the end of range of the ^3He ions (see Fig. 3.13). For temperatures between 300-700 K, it is expected that these traps will mostly be vacancies, dislocations, and small vacancy clusters [71, 70]. Trap production may be less efficient in regions of higher dpa due to increased probability of the displacement being filled with a non-D interstitial [70, 49], and that trap production per dpa may be less efficient near the end of range of the 3.5 MeV ^3He ions since the probability of the trap being filled with ^3He will increase [70]. These factors, combined with the fact the produced traps

Figure 3.14 An IR Image of a deuterium plasma incident on a glass plate. The IR reflection is IR emission from the helicon quartz tube reflected off the glass plate.

are likely to be mobile [71], will produce a trap distribution that is not nearly as peaked as the dpa distribution seen in Fig. 3.13. Recall that Takagi et al found a conversion factor of 0.007 for dpa to traps assuming a linear relation between the two [49]. Since the ^3He ions are in the high energy range (>1 MeV), it is unlikely there will be significant surface blistering caused by the ion beam as was seen in experiments of intermediate energies ($10 \text{ keV} < E_\alpha < 1 \text{ MeV}$) [72, 74].

The DIONISOS experiment also has an IR thermal camera that can measure surface temperature in real time across the entire plasma column (see Fig. 3.14). This diagnostic not only gives accurate reading of surface temperature but also the temperature profile of the plasma column can also indicate the plasma heat load, and assuming equal energy for all plasma ions, this can be used as a measurement of plasma flux as a function of radius. Based on Fig. 3.14, the column appears to have a diameter of ~ 2 cm and a peaked flux profile with the maximum at the center of the column as was seen with the Langmuir probe in section 3.1.2. IR reflections can make IR imaging for near RT samples difficult. In the helicon plasma source, a great deal of UV light is emitted. This UV is absorbed into the chamber walls and viewport windows and these components will begin to

heat up and emit IR radiation. The IR radiation from components such as quartz or glass windows that have a very high emissivity can dominate the IR signal from a Mo plate that is $<100\text{ }^{\circ}\text{C}$. This makes it important to have the IR thermal imager properly calibrated for the experiment.

Other surface diagnostic techniques are available through the Department of Material Science & Engineering. X-ray photoelectric spectroscopy (XPS) is used to determine the elemental composition of the first few nanometers of a surface. Scanning electron microscopy (SEM) is used to visually inspect surfaces for damage or defects such as blisters. A Zygo Interferometer is also used to measure more macroscopic ($>1\mu\text{m}$) features.

In section 2.3, it was mentioned that TDS is a valuable tool when studying hydrogenic trapping and retention. A TDS system is nothing more than a method of heating the sample and an RGA to analyze the outgassed particles. Although DIONISOS does not have a RGA system in place, the sample is mounted on a heatable sample holder. The maximum temperature for a sample in DIONISOS is 800 K. Other TDS systems heat samples to 1200-1400 K. The lower maximum temperature in DIONISOS can be compensated for by having a faster temperature ramp rate. This should allow for hydrogen and deuterium to be completely outgassed from the Mo samples. An RGA can easily be added to the pump system for the vacuum vessel. This is something that can be considered for DIONISOS in the future. For the present study, NRA can be used to monitor the D inventories in the specimens as the temperature is increased and, in fact, provide depth profile information during the temperature ramp, which further informs one about the mobility and release of the D from the sample.

3.3 Specimens and Specimen Preparation

In total, there have been 5 types of specimens used for this work. The majority of the work was performed on polycrystalline Mo plate with a thickness of 1.5 mm, there were two batches of this Mo plate used for samples. A 25 μm Mo foil was used for exposures to investigate blister formation. The Mo foil had a smooth, mirror finish, making features $<1\mu\text{m}$ in size, such as surface blisters, easily discernible on a SEM. The surface roughness of the Mo plate made it unsuitable for SEM images of small features. Fig. 3.15 shows examples of the Mo plate and the Mo foil.

Figure 3.15 Examples of the Mo plate and Mo foil used in DIONISOS.

Additional work was performed on a tungsten (W) lamellae sample and a ultra-sonically cleaned Alcator C-Mod tile.

The Mo plate came in two batches, Batch A and Batch B. Both batches were purchased from Ed Fagan Inc. where they were fabricated by powder sintering and are 99.97 % pure. For detailed impurity analysis see Table 3.2. Batch A came in pre-cut pieces of $10\text{ cm} \times 10\text{ cm}$. These plates were installed into DIONISOS in the “as is” condition, meaning there was no surface polishing before exposure. The plates are bolted to the heat sink with bolt holes at each corner, as far removed from the plasma spot as possible. To improve thermal contact, a sheet of Grafoil (flexible carbon sheet designed to improve thermal contact between two flat surfaces) was secured between the Mo plate and the heat sink. Batch B was cut at the University of Wisconsin-Madison into pieces that were $3.8\text{ cm} \times 3.8\text{ cm}$. Since these pieces could not be bolted directly to the heat sink, a mask was made to compress the smaller Mo pieces between the heat sink and the mask. The mask was made from a 0.3 cm thick Mo plate and had a 2.5 cm diameter hole cut in the center. The mask could be bolted directly to the heat sink and was used to accommodate smaller samples in DIONISOS. Grafoil was also used with the Mo sample from Batch B. The Mo foil was purchased from Elmet technologies in $30.5\text{ cm} \times 30.5\text{ cm}$ sheets. It is polycrystalline Mo and was also fabricated via

powder sintering and is 99.90 % pure (see Table 3.2). Scissors were used to cut the large sheets into smaller samples. The Mo foil is first attached to a Mo plate from Batch B with double-sided, heat conductive copper tape. This is then attached to the heat sink using the Mo mask and Grafoil to improve thermal conductivity.

The W lamellae sample received from MIT was 4 mm thick and cut to 3.8 cm $\times$ 3.8 cm dimensions. The lamellae structure consists of many thin W sheets being rolled together to form a thicker plate. This lamellae structure can lead to large grain boundaries parallel to the lamellae sheets. For this sample, the lamellae sheets were oriented parallel to the surface. The surface was roughly polished before being shipped to the University of Wisconsin but no other polishing was performed once it was received. The tungsten is 99.97 % pure (see Table 3.2). The W lamellae was attached to the heat sink using the Mo mask and a Grafoil backing. Because of the extra thickness of this sample, washers were used between the Mo mask and the copper heat sink to prevent any bending of the heat sink plate.

An Alcator C-Mod tile was obtained from MIT for analysis in DIONISOS. At MIT, the face of the tile was cut off the bulk creating a 4 mm thick sample with one side that was plasma-facing in Alcator C-Mod. To recreate the same surface conditions as in Alcator C-Mod during their bare Mo wall campaign [22], the boron deposits on the plasma-facing surface of the tile needed to be removed. Following the same procedures as were used at C-Mod, the tile was first wiped with distilled water until the wipe came away clean. Next, the tile was ultra-sonically cleaned in distilled water at a temperature of 50°C for 2 hours. After removing the tile from the bath, it was cleaned with alcohol and baked in vacuum at 200°C for 30 minutes to remove all water absorption. The Alcator C-Mod tile was attached to the DIONISOS heat sink in the same manner as the W lamellae sample. The exact chemical purity of the C-Mod tile is not known but is thought to be similar to Batch A and B of the Mo plate samples. From previous work, it is known that these cleaning procedures can still leave 10-15% boron in the first micron of the Mo.

Besides the cleaning of the Alcator C-Mod tile, there were no special surface treatments for experimental specimens. All foils and plates were thoroughly cleaned with alcohol before being installed in DIONISOS but, as mentioned, the surfaces were left in the “as is” condition. The one

Impurity	Mo Batch A	Mo Batch B	Mo foil	W lamellae
Al	8	8	25	15
Ca	2	2	20	5
Cr	13	13	20	20
Cu	8	8	10	10
Fe	14	12	50	30
Mg	2	2	10	5
Mn	3	3	-	5
Ni	11	16	50	5
Pb	10	10	10	5
Si	15	15	300	20
Sn	15	15	20	-
Na	5	5	20	10
K	19	12	150	10
C	10	10	50	30
Ti	10	10	-	5
O	28	18	200	20
N	10	10	20	5
W	130	120	300	99.97%
Mo	99.97%	99.97%	99.90%	100%

Table 3.2 Impurity concentrations in parts per million by weight for Mo and W samples.

exception was one of the Mo plates from Batch B was polished thoroughly for a plasma exposure in DIONISOS to search for surface blistering at high temperatures (see section 4.6). It was found that rough sanding of a surface could eliminate any D inventory trapped in the surface. However, all of the results presented in chapter 4 (with the exceptions listed above) were performed on "as is" surfaces.

Chapter 4

Experimental Results

The following chapter presents the experimental results obtained on the DIONISOS experiment (excluding the surface analysis techniques in sec. 4.6). They are presented in the manner that is easiest to follow but was not necessarily the order in which the data was obtained.

4.1 Ion Beam Trap Production

4.1.1 Ion Beam Effects

It is clear from the literature that the irradiation of the Mo targets with the ion beam will produce trap sites and affect the retention properties of the Mo. So, it is important to isolate the ion beam effects and this should allow us to better understand the role the plasma is having in terms of trap production and D retention. This is important for comparing our results to current fusion experiments such as Alcator C-Mod where MeV-range particles are not generally present.

The easiest way to isolate the beam effect is to have one plasma exposure with the ion beam simultaneously irradiating the target and one plasma exposure where the ion beam was removed from the chamber. This was performed at a temperature of 500 K to ensure the the retention in the first 5 μm of the surface was not diffusion limited. All exposure conditions can be found in Table 4.1. The results show that the irradiated and un-irradiated exposures produce similar depth profiles but different total retention values (see Fig. 4.1). The total retention in the irradiated case is $3.9 \times 10^{20} \text{ D/m}^2$ and the total retention in the un-irradiated case is $0.44 \times 10^{20} \text{ D/m}^2$. This implies that 80-90 % of the traps are created by irradiation. It also shows that the plasma exposure is producing traps and these trap sites are found much deeper than the plasma ion implantation range. So, it

Figure 4.1 Deuterium depth profiles for irradiated and un-irradiated Mo targets at 500 K after a 100 eV plasma exposure.

Figure 4.2 A comparison of spectra taken from an irradiated location (center) and an unirradiated location (~ 1 cm off-center) on a Mo plate at 400 K after a 100 eV plasma exposure.

Parameter	Irradiated Exposure	Un-irradiated Exposure
T_{Mo}	500 K	500 K
E_{D+}	100 eV	100 eV
E_{3He}	3.5 MeV	-
Exposure time	1500 s	1500 s
D+ fluence	1.5×10^{24} D/m ²	1.5×10^{24} D/m ²
³ He fluence	4.4×10^{20} ³ He/m ²	0 ³ He/m ²

Table 4.1 Plasma and surface conditions for irradiated and un-irradiated exposures.

appears that both the ion beam and the plasma are producing trap sites and that these trap sites are mobile. A similar experiment was performed to examine the ratio of trap production between the ion beam and the plasma, except in this test, the irradiated and un-irradiated data was taken from the same specimen after a single plasma exposure. The irradiated data was taken from the point where the ion beam was striking the target, at the center of the plasma column. The un-irradiated data was taken from a point ~ 1 cm off-center of the plasma column and away from the ~ 4 mm diameter irradiating beam spot. This experiment was conducted at a Mo temperature of 400 K as opposed to 500 K for the results seen in Fig. 4.1. One must remember that points off-center of the plasma column also receive lower plasma fluxes (see Fig. 3.7). Using the spatial profile from Fig. 3.7 to determine the plasma flux density at the off-center location, the results for both the irradiated and un-irradiated locations have been normalized to the incident D fluence. The results show a difference of a factor of 2-3 between the data on the irradiated and un-irradiated targets indicating that the plasma produces 30-40% of the traps in this case (see Fig. 4.2). From the shapes of the profiles, it is clear that the plasma is producing traps down to the end of the detection range. The difference in the percentage of the plasma-produced traps as a fraction of the total traps may be an indication of a temperature dependence for trap production of either the ion beam, the plasma or both.

4.1.2 DPA vs D Retention

While it is clear that damage from high-energy particles increases deuterium trapping in Mo (see sec. 4.1.1 and [49]), it is important to be able to quantify how damage translates into deuterium traps. The easiest way to quantify damage is to use displacements per atom (dpa) which can be accurately predicted with the TRIM code if the experimental parameters are well known. The amount of dpa is linearly dependent on the total ^3He fluence. This ^3He fluence can be controlled by varying the ion beam current for the exposure. The beam current can only be lowered so much before it becomes too difficult to monitor in the RF plasma environment.

The presence of traps is measured directly by NRA assuming the traps are 100 % filled. So, by varying the dpa by changing the beam current and then measuring the trap density with NRA after the plasma exposure, it is possible to plot traps produced vs. dpa and this should translate into a conversion between dpa and traps. NRA measurements were taken for dpa levels of 0, 0.67, 1.11, 1.40, and 1.75 dpa. The exposure conditions are listed in Table 4.2. All Mo targets were from Batch B of the Mo plate (see Table 3.2).

The data shows that, while saturation has not occurred, there appears to be a trend of trap production slowing down as dpa is increased (See Fig. 4.3). Despite the appearance of this trend, if 10% error bars are added to the data, there are several functions of dpa that yield valid fits of

Parameter	0	0.67 dpa	1.11 dpa	1.40 dpa	1.75 dpa
T_{Mo} (K)	500	500	500	500	500
E_{D+} (eV)	100	100	100	100	100
$E_{^3He}$ (MeV)	-	3.5	3.5	3.5	3.5
Exposure time (s)	1500	1500	1500	1500	1500
D+ fluence (D/m^2)	1.5×10^{24}	1.5×10^{24}	1.5×10^{24}	1.5×10^{24}	1.5×10^{24}
^3He fluence ($^3\text{He}/\text{m}^2$)	0	1.7×10^{20}	2.8×10^{20}	3.5×10^{20}	4.4×10^{20}

Table 4.2 Plasma and surface conditions for 0, 0.67, 1.11, 1.40, and 1.75 dpa Mo target exposures.

Figure 4.3 The trap densities, as measured by NRA, as a function of dpa in the Mo target. There are several functions that yield acceptable fits to the data.

the data. Among these fits is a linear fit (Trap density = $0.0007(dpa)+0.0003$) that would imply there is no hints of saturation in the data. However, there is also a square root fit (Trap density = $0.001(dpa)^{1/2}+0.000135$) and a fourth root fit (Trap density = $0.001(dpa)^{1/4}+0.000135$) that are in better agreement with the data and would indicate a trend toward saturation. A key feature is that for dpa ~ 0.5 , substantial increases in H/D/T retention are expected. Such levels of neutron-caused displacements will occur in less than two weeks of operations in a typical fusion reactor, where damage levels of 20 dpa/year are expected. Given that the literature shows evidence of both saturation [68, 69] and non-saturation [49], the best fit for Fig. 4.3 may be best answered through modeling (see Chapter 5).

4.2 Deuterium Retention as a function of Surface Temperature and Plasma Ion Energy

4.2.1 Experimental Procedure and Exposure Conditions

Due to the strong temperature dependence of diffusion, surface recombination and thermal detrapping of D in Mo, the temperature dependence of hydrogenic retention in Mo is one of the most important factors in determining the physics of the processes. In this study, experiments were run at Mo temperatures of 300, 400, 500, 600, and 700 K.

Plasma ion energy is an important parameter to determine how the plasma is affecting the surface. In a tokamak, the incident ion energy to the wall can vary from <10 eV for detached plasmas to $\sim$ keV from sheath rectification from ICRF antenna near the plasma edge [78, 79]. According to TRIM simulations, D ions with energy ≥ 350 eV will begin to produce vacancy sites due to energy transfer to lattice Mo atoms (lattice binding energy of 30 eV is assumed). At ~ 100 eV, common plasma impurities such as carbon, boron, and oxygen are capable of creating displacements in the surface by energy transfer but the D ions can not. At energies below 50 eV, there should be no plasma ion that would be capable of creating displacements in the surface. To cover the range of situations possible in a tokamak, data is taken at ion energies of 30, 100, and 350 eV. Notice that we have already shown that D ions with energy of 100 eV can produce traps in Mo (see sec. 4.1.1) and this will be discussed further in Chapters 5 and 6, but it is clear that a process other than physical collisions/energy transfer must be involved.

Plasma ion energy will also strongly influence the Mo sputtering from D ion impact. From the ALADDIN database [80], the Mo sputtering yield for D ions with energy ~ 100 eV is $\sim 10^{-5}$ Mo/D⁺ and the sputtering yield for D ions with energy <100 eV is zero. However, for 350 eV D⁺, the sputtering yield ranges from 0.002-0.006 depending on which model one uses [80]. These sputtering yields could lead to significant erosion of the surface during lengthy plasma exposures.

There are 5 different samples used for these experiments. Three Mo plates from Batch A are used, one for each ion energy (30, 100, and 350 eV) as well as the Alcator C-Mod tile and the W tile (see sec. 3.3). The general experimental procedure was the same for all specimens.

All temperatures were performed in order beginning at 300 K and ending at 700 K for each ion energy, with the exception of the W tile, which was only exposed at 400 K. Initially, the target would be brought up to the desired temperature and the D content of the Mo specimen would be measured with NRA. The plasma would be turned on and the ion beam would continue to monitor the dynamic inventory through NRA, and irradiate the target. Once the plasma was turned off, the sample temperature was maintained at the selected value and the D inventory was measured for a time equivalent to that of the plasma exposure. Finally, one last D inventory measurement would be made after a period of 1000 s when it was assumed the system had reached a new equilibrium. After all measurements were made, the D would be thermally desorbed from the sample (see sec. 4.3 for details) and the entire process could be repeated at another temperature. Because the same specimen was used for all temperatures (but only a single ion energy), a history effect could be playing a role in the results. For comparison purposes, any history effect was minimized by following the same procedures and temperature order for each specimen. For the 30 eV data, there were additional temperature spectra taken for 700, 500, and 600 K (in that order) after initial spectra were acquired for all temperatures (300-700 K). These spectra were taken because of uncertainties or instabilities in either the ion beam or the plasma during the previous 30 eV exposure at that temperature. This also provides a test for history effects at those temperatures.

The experimental parameters were kept constant to within 10% with the exception of the 100 eV Mo plate data. For the 100 eV data, the ion beam current was run much lower than all other experiments due to instability with the ion accelerator at that time. Also, the plasma ion flux density was higher (it was reduced for all other experiments to improve ion beam control and stability in the RF plasma environment). These two factors combined means the 100 eV data was taken with a shorter exposure time, to keep the total D ion fluence constant with results from the other ion energies, and with lower time resolution (the time to acquire a single NRA energy spectrum), to compensate for the lower ion beam currents. It is important to remember that lower ion beam current and exposure time will mean fewer beam produced trap sites for the 100 eV data. The full set of typical experimental parameters for all specimens examined can be found in Table 4.3.

Parameter	30 eV Mo	100 eV Mo	350 eV Mo	30 eV C-Mod	30 eV W
T_{target} (K)	300-700	300-700	300-700	300-700	400
E_{3He} (MeV)	3.5	3.5	3.5	3.5	3.5
Exposure time (s)	1500	1000	1500	1500	1500
Time resolution (s)	250	300	250	250	250
D+ fluence (D/m ²)	1.5×10^{24}	1.5×10^{24}	1.5×10^{24}	1.5×10^{24}	1.5×10^{24}
³ He fluence (³ He/m ²)	4.4×10^{20}	2.4×10^{20}	4.4×10^{20}	4.4×10^{20}	4.4×10^{20}

Table 4.3 Plasma and surface conditions for 30, 100, and 350 eV Mo exposures, 100 eV Alcator C-Mod tile exposure, and 100 eV W exposure.

4.2.2 D Retention Profiles measured by IBA

The NRA technique provides deuterium concentration as a function of depth and also total D retention up to the detection depth of the incident ion beam, in this case $\sim 5 \mu\text{m}$. The following sections present results of D depth profiles and total D retention in the first $5 \mu\text{m}$ of the surface of pure Mo (Mo plate, Batch A), an ultrasonically cleaned Alcator C-Mod tile, and a W lamellae specimen. For detail on the specimens and specimen preparation see sec. 3.3.

The temperatures will be categorized into three regimes: Room Temperature (300 K), Intermediate Temperatures (400 K and 500 K), and High Temperatures (600 K and 700 K). These different temperature regimes correspond to different retention behaviors as will become clear in the following sections.

4.2.2.1 Pure Mo

All un-exposed specimens of the Mo plate had an initial D concentration of $\lesssim 10$ appm but exposed specimens that undergo thermal desorption in DIONISOS will typically have D concentrations of ~ 100 appm before the next plasma exposure. This initial D concentration is small ($<10\%$) when compared to D concentrations after plasma exposure.

Figure 4.4 The D retained as a function of Mo temperature and plasma ion (D+) energy in the first 5 μm of the Mo plate specimens. The retention levels plotted are only for the first 5 μm of the surface, the D detection limit for NRA. Much of the retention for the 600 K and 700 K cases occurs past 5 μm , making the values shown on this graph minimum values for the total retention at these temperatures.

The results for the total D retention in the first 5 μm of the surface can be seen in Fig. 4.4. These results are based on the final NRA spectrum taken before the plasma was turned off for that exposure. All temperature measurements for the Mo plates are presented for all energies. The repeated temperatures in the 30 eV case are labeled as "re-do".

The depth profile of the deuterium concentration also yields valuable information about the retention characteristics. The depth at which the D is trapped affects how easily the D is removed by thermal desorption. The depth profile can also help determine the role and quantify the rate of diffusion of D through the surface of the Mo specimens. The D depth profiles are separated into room temperature (Fig. 4.5), intermediate temperatures (Fig. 4.6), and high temperatures (Fig. 4.7). The room temperature profile appears to be diffusion-limited, but show D concentration near

Figure 4.5 Deuterium concentration as a function of depth for all ion energies at Mo temperature of 300 K.

the surface of $\sim 1\%$ (i.e. much higher than any intrinsic trap density or hydrogenic solubility for Mo). Intermediate temperatures show a deuterium gradient into the surface and high temperatures show a flat or close-to-flat deuterium profile implying very deep penetration of the D into the surface. Because the deuterium concentration is non-zero at the end of detection range ($5 \mu\text{m}$) for intermediate and high temperatures, it is assumed there is deuterium trapped deeper in the Mo. This makes the retention values shown in Fig. 4.4 minimum retention values with the true values likely to be significantly higher.

Figure 4.6 Deuterium concentration as a function of depth for all ion energies at Mo temperatures of a) 400 K and b) 500 K.

Figure 4.7 Deuterium concentration as a function of depth for all ion energies at Mo temperatures of a) 600 K and b) 700 K.

4.2.2.2 C-Mod tile

The Alcator C-Mod tile was exposed to the same conditions and procedures in DIONISOS as the Mo plate. The main difference was there was a layer of boron and Mo on the surface. Prior to any plasma exposure in DIONISOS, NRA analysis found this layer to contain 12% B and was $\sim 0.5 \mu\text{m}$ thick. In this layer, a D fraction of 0.007 D/Mo was measured. The source of this deuterium will have been from Alcator C-Mod plasma discharges during the tiles time as a PFC for that device. Despite repeated thermal desorptions up to 720 K and plasma exposures, this $0.5 \mu\text{m}$ layer remained unchanged to within 5% both in terms of thickness and elemental composition. Since this layer is unaffected by conditions in DIONISOS it can be subtracted as a background. Results in which the background signal is subtracted will be labeled "net" and results which include this background signal will be labeled "total".

The results for the total D retention over the first $5 \mu\text{m}$ of the surface of the C-Mod tile can be seen in Fig. 4.8. It is clear that the D retention is lower than was seen for the pure Mo plate. This a counter result to the usual assumption that low-Z materials will always enhance retention in a tokamak. The cause for this difference can be seen in the D concentration depth profiles for the Alcator C-Mod tile (see Fig. 4.9). It is clear that the D from the plasma is trapped at the surface and has limited access to the trap sites created deeper in the surface from the ion beam irradiation.

4.2.2.3 W Specimen

The W specimen is intended to connect the work done in this study to those fusion devices, both present and future, that use W as a first-wall material. Although Mo and W are similar in their thermo-mechanical properties and atomic structure, it is not clear if their retention properties are similar as well. The goal for the W specimen was to retain as much D as possible, so the exposure conditions for maximum D retention in Mo were chosen ($T_{mo}=400 \text{ K}$, $E_{D+}=30 \text{ eV}$, see Fig. 4.4). Before the plasma exposure, the D content was $\lesssim 10 \text{ appm}$, similar to what was found in the Mo plate specimens.

After the plasma exposure, the retained D in the W was measured to be $3.25 \times 10^{20} \text{ D/m}^2$. This is the lowest retention of all the specimens measured, including the Alcator C-Mod tile. Clearly, the

Figure 4.8 The D retention in the first 5 μm of the Alcator C-Mod tile as a function of temperature. The 30 eV/D+ results for the pure Mo plate are included for comparison purposes.

Figure 4.9 Total deuterium concentration as a function of depth for all temperatures for the Alcator C-Mod tile.

Figure 4.10 Deuterium concentration as a function of depth for W lamellae specimen at 400 K.

retention behavior of this W lamellae specimen is much different than that of the Mo plate. Again, the depth profile of the deuterium concentration (see Fig. 4.10) leads to a possible explanation. Clearly, the retention is diffusion-limited. The implanted D from the plasma can not access the traps available deeper in the W specimen. Because the retention in the first 5 μm at 400 K for the Mo plate specimens was not diffusion-limited, this implies a higher activation energy for diffusion for W than for Mo.

4.2.3 Discussion

When examining the retention values and depth profiles for the Mo plate specimens (see Fig. 4.4 and Fig. 4.5), two observations can be made immediately. First, the highest retention occurs at intermediate temperatures and the lowest retention, taking into account that significant retention may be occurring beyond the detection depth for high temperatures, is likely to be at room temperature. This result is very contradictory to what is found in literature where retention at room

temperature is typically highest [51, 42, 45] with retention decreasing with increasing temperature. The main difference between the current study and past results is the presence of the ion beam during plasma exposure. This target irradiation creates trap sites several microns into the surface and this allows D that has diffused deeper into the surface to have access to available trap sites. If the ion beam were not present, as in past experiments, the D could still diffuse deep into the surface, but with no empty traps available, the D will remain in solution until it reaches a surface, recombines and is released.

The second observation is that plasma ion energy appears to have no effect on either total D retention or the D depth profiles. The fact that there is no difference between retention between 30 eV and 100 eV D⁺ ions can be explained if there are very few plasma impurities. Since plasma impurities can create displacements in Mo at 100 eV but not at 30 eV, it must be assumed that plasma impurity impact on the Mo surface is not having a significant impact on the retention characteristics of the Mo. At 350 eV, D⁺ ions from the plasma can create displacements in a Mo surface. One would assume that this would translate to the production of trap sites and an increase in retention with the increase in ion energy. Since there is no increase in retention at 350 eV, this implies the number of trap sites produced by the D⁺ ions through energy transfer with the surface is not significant in comparison to another trap production mechanism. We know the plasma does create traps from the work shown in sec. 4.1 but, because of the lack of ion energy dependence on retention, it is unlikely that these traps are made through ion impact on the surface. The hypothesis for this study is that the plasma-induced traps are pressure-driven rather than energy-driven.

By operating DIONISOS at high plasma flux densities of low-energy D⁺ ions, a large number of D atoms are implanted across a depth of only a few nanometers. Since the solubility of D in Mo is very small (see sec. 2.2) there is limited interstitial space for the D to reside and the rate at which the D can diffuse out of the implantation region will be limited somewhat by the temperature of the Mo. Combine all of these factors and it results in a build-up of very large pressures and stresses in the implantation region. Dislocation and vacancy production could be a mechanism by which these stresses are relieved. This would mean that the plasma would be able to produce traps in the surface of the Mo by means that depend very weakly on the incident ion energy (the ion energy

would only determine the straggle length of the implantation, determining the volume over which the ions are implanted) and strongly on the incident flux density of the plasma ions. Unfortunately, no controlled study of flux density dependence was made in this study, however, the different experimental conditions used for the 100 eV plasma exposures (see Table 4.3) can be used to give some insight on any dependence of D retention on incident plasma flux density. Recall that the 100 eV plasma exposures operated at a flux density 50% higher than for the 30 and 350 eV exposures. The 100 eV exposures also had $\sim 40\%$ lower ion beam current irradiating the target during the plasma exposure (see sec. 4.2.1 and Table 4.3). The lower ^3He ion fluence and shorter exposure time will translate into fewer traps produced by irradiation as was shown in sec. 4.1.2. This translates into $\sim 50\%$ fewer beam-produced traps for the 100 eV exposures. Since the ion beam appears to create 80-90% of the total number of traps, this should lead to a decrease in retention. However, the results show that the retention for the 100 eV exposures is very similar to that of the other energies for all temperatures. The only other difference is the increased plasma flux density of the 100 eV exposures. *It would appear that this increased flux density has increased the plasma-induced trap production such that the loss of beam-produced traps is compensated.* This would support the hypothesis of pressure-driven trap production by the plasma. This is examined further with modeling in Chapter 5.

The retention value for the Mo plate 30 eV "re-do" exposure at 500 K suggests a history effect is present in the process of repeatedly irradiating, exposing and thermally desorbing the specimens. The retention for the 500 K "re-do" exposure is $\sim 50\%$ higher than the retention result for the original exposure at that temperature. There were 3 repetitions of the experimental procedure between these two exposures and the increase in retention may be due to a build-up of irradiation damage that has not been fully annealed from the sample during the thermal desorption. This same effect is not seen to the same degree at temperatures of 600 and 700 K, but this may have to do with saturation conditions at these temperatures.

Fig. 4.6 shows the D depth profile is peaked at the surface for intermediate temperatures. This is despite the fact that the irradiation from the 3.5 MeV ^3He beam produces a damage profile that is peaked at a depth of $\sim 4.5 \mu\text{m}$. This clearly indicates the ability of beam-produced traps to

migrate. The results from Takagi et al [49] showed a peaked distribution of D that was similar to the damage distribution from 0.8 MeV ^3He irradiation but that trap migration and other factors, such as the increased probability of a vacancy being filled by a non-D interstitial in regions of higher dpa, caused the D depth profile peak to broaden. It is clear that the present results do not resemble those obtained by Takagi et al. There are several factors that could explain the difference in results. The irradiation by Takagi et al has a sharper, higher peak of dpa distribution due to the lower ^3He energy. The details of their plasma exposures are unknown and the plasma-produced traps in DIONISOS experiments, which will be created very close to the surface, may contribute to the current results being peaked at the surface.

The comparison of the Mo plate exposures to the Alcator C-Mod tile exposures and the W lamellae exposure show the retention properties of these specimens to be very different from one another (see Fig. 4.11). The D retention for the Alcator C-Mod tile is a factor of ~ 5 lower than for the pure Mo plate for intermediate temperatures. This is due to the fact that the D retention of the Alcator C-Mod tile does not show the same enhancement of retention at intermediate temperatures that was seen for the Mo plate. This is a surprising result considering the high D retention that was seen in Alcator C-Mod while using these ultrasonically cleaned Mo tiles as a first wall (see sec. 1.3). The W lamellae specimen shows even lower D retention than the Mo plate and the Alcator C-Mod tile at 400 K.

The differences in D retention for these different specimens is made more clear when the D depth profiles are compared (see Fig. 4.12-4.14). The depth profiles shows that the D is much more mobile in pure Mo than in the Alcator C-Mod tile or the W lamellae specimen for this temperature. The D is concentrated mostly in the Mo and B layer at the surface of the Alcator C-Mod tile. There is D trapping deeper into the surface but to a much lesser extent than the pure Mo plate. This limits the total retention of the Alcator C-Mod tile. The deuterium is even less mobile in the W lamellae specimen. Because the deuterium can not access the deeper traps caused by the irradiation, the overall D retention goes down. It should be noted that the surface temperature of divertor plates in C-Mod will likely surpass the 700 K limit of these experiments, and that D diffuses more easily through the permeation barrier in those cases.

Figure 4.11 A comparison of the D retention in the first 5 μm of the surface as a function of temperature between a pure Mo plate, an Alcator C-Mod tile, and a W lamellae specimen.

Figure 4.12 A comparison of the D concentration depth profile at 300 K for a pure Mo plate and an Alcator C-Mod tile specimen.

Figure 4.13 A comparison deuterium concentration as a function of depth for 30 eV ion energy between a pure Mo plate, an Alcator C-Mod tile, and a W lamellae specimen for temperatures of
 a) 400 K and b) 500 K.

Figure 4.14 A comparison deuterium concentration as a function of depth for 30 eV ion energy between a pure Mo plate and an Alcator C-Mod tile specimen for temperatures of a) 600 K and b) 700 K.

The reduced diffusion can be expected in the Alcator C-Mod tile since it has been shown that small amounts of boron and carbon can reduce the diffusion of deuterium in Mo [41, 6]. So a region that is 12% boron will have greatly reduced D diffusion. The location of the boron may also play a role in its effect on the diffusion of deuterium. If the boron is collected in the grain boundaries on the surface, it reduces the diffusion even more by eliminating the accelerated diffusion that is made available by grain boundaries. It is concluded that the boron that is responsible for the strongly inhibited diffusion in the surface region that is seen in the Alcator C-Mod tile.

The low diffusion rate for the W lamellae at 400 K is unexpected. From the accepted diffusion rate from Frauenfelder [38] for W at 400 K, the diffusion should be $5.0 \times 10^{-12} \text{ m}^2/\text{s}$. For a 1500 s exposure, the characteristic length scale for D diffusion is $\sim 85 \text{ } \mu\text{m}$. This would indicate that the D diffusion should not be a limiting factor for W at this temperature. Since we are dealing with 99.97% pure W (see Table 3.2), it is unlikely that impurities are inhibiting diffusion as was the case in the Alcator C-Mod tile. The surface of the W lamellae was polished before being received at the University of Wisconsin-Madison. This presents two possible explanations to the apparently low diffusion rate. First, the polishing may have disordered the surface in such a manner as to greatly reduce the diffusion. Second, since the W is a lamellae structure, it is possible that a lamellae boundary is located at a depth of $\sim 2 \text{ } \mu\text{m}$. The lamellae layers are much thicker than $2 \text{ } \mu\text{m}$, but it is possible that the polishing of the surface has reduced the thickness of the first lamellae layer to $\sim 2 \text{ } \mu\text{m}$. Zakharov et al have published a H diffusion rate in W that has a much higher activation energy for diffusion (1.07 eV) than the activation energy found by Frauenfelder (0.41 eV) [32]. If the diffusion rate from Zakharov et al is used, the characteristic length for diffusion for a 1500 s exposure would be $\sim 75 \text{ nm}$. So if that activation energy were used, it would not be surprising that the hydrogenic retention of D in W was diffusion limited at 400 K.

Even ignoring the low diffusion rate of the D in W, the D retention in the surface layer is still lower than is observed for pure Mo. This may indicate a higher resilience of W to either irradiation or pressure-induced trap production, or both. This would make W a more favorable PFC material than Mo since it's apparent resilience to irradiation and plasma-produced traps gives it more desirable hydrogenic retention properties. This should be a topic of future studies.

4.3 Thermal Desorption

The thermal desorption in DIONISOS is mainly to remove the deuterium from the surface so repeated plasma exposures can be performed on the same target. However, thermal desorption can also be useful in determining how strongly and possibly how deep the deuterium is trapped in the surface (see sec. 2.3). In DIONISOS, the thermal desorption is not monitored by an RGA as is normal, it is monitored with NRA. NRA provides depth profiles during desorption, but lacks the ability to provide a "global" accounting of D released. This is a less accurate and precise method but can still yield useful results.

4.3.1 Experimental Procedure

Thermal desorption is the process of de-trapping, diffusion to a surface, and recombination to be released from that surface. This means that thermal desorption is occurring at all temperatures, but depending on the limiting process, it may be insignificant at lower temperatures. In the experimental procedure for plasma exposures in DIONISOS, thermal desorption is a competing process against ion implantation from the plasma. However, when the plasma is turned off and the specimen temperature stays elevated, thermal desorption then becomes the major process that affects the deuterium inventory in the surface.

Thermal desorption takes place after the plasma is turned off until the end of the data acquisition process and also after all data is acquired, the specimen temperature is raised in step-wise fashion to accelerate the desorption process so the next plasma exposure can be performed without delay. The temperature would be stepped from 370 K to 670 K in steps of 100 K and finally from 670 K to 720 K. At each step a NRA spectrum would be taken to monitor the D content of the surface. It would take 100-300 s to step from one temperature to the next and the temperature at each step would be held for ~ 300 s. The specimen temperature would be held at 720 K until the D content of the surface was $\lesssim 100$ appm.

Figure 4.15 The D depth profiles at the temperature steps for a thermal desorption after a Mo plate exposure with $T_{mo}=300$ K and $E_{D+}=30$ eV.

4.3.2 D Desorption Profiles measured by IBA

The behavior of the deuterium in the Mo plate was the same for all exposures no matter what the plasma ion energy or Mo temperature was for that plasma exposure. This behavior is best demonstrated by plasma exposures at 300 K where the D is initially trapped close to the surface (see Fig. 4.15). For the purposes of comparison to the W lamellae and Alcator C-Mod tile, the 30 eV case will be used. Fig. 4.15 shows that the total D content not only decreases in the first 5 μm of the surface but the D that was trapped near the surface initially, now has access to traps deeper in the surface as the temperature is increased. The effect of the thermal desorption is two-fold. First, the total D content is decreased as temperature is increased. Second, the depth profile of the D concentration flattens as the temperature increases. Once the depth profile is flat, the D content continues to decrease but the depth profile no longer changes. The Alcator C-Mod tile has been shown to have reduced diffusion. This will also affect the thermal desorption characteristics.

Similar to the depth profiles for the Alcator C-Mod tile plasma exposures, as the temperature is stepped up, the deuterium has only limited access to the deeper traps in the surface (see Fig. 4.16). The majority of the reduction in D content is from the boron-rich surface layer. However, a small amount of D diffuses beyond this layer. The D that is past the boron-rich surface layer is difficult to thermally desorb because of the steep D concentration gradient at the surface. This makes it much more likely to diffuse deeper into the sample than back to the surface. This D is also in a region with many empty trap sites created by the irradiation. This means there is a greater probability for the D to fall back into a trap site after being de-trapped from another. This continuous falling in and out of traps is likely to inhibit thermal desorption, making the D trapped deep in the Alcator C-Mod tile more difficult to thermally desorb than a pure Mo plate.

The W lamellae appeared to have a lower than expected diffusivity of D for the exposure at 400 K. One possible explanation for that was that the diffusion rate of Frauenfelder was wrong and that the diffusion rate from Zakharov was more accurate at the temperatures. If this is the case and the activation energy for diffusion is closer to the value found by Zakharov than by Frauenfelder, as the temperature is stepped up, the D trapping should no longer be diffusion limited and should be able to access the traps to the end of detection range. Fig. 4.17 shows that this is not the case. Despite stepping up the temperature to 720 K, the deuterium is still confined to the first $\sim 2.5 \mu\text{m}$ of the surface. This suggests that there is something actively inhibiting the diffusion. The exact cause of the inhibition is not known but the best guess is that the lamellae structure of the W is responsible.

4.3.3 Discussion

Since for thermal desorption, the detrapped D needs to diffuse to a surface before it is released, diffusion plays a major role in desorption behavior. Therefore, it is not surprising that for the pure Mo thermal desorption, the D density gradient first flattens and then reduces uniformly. Since diffusion can not take place up a gradient, the gradient will flatten as the more plentiful D near the surface become de-trapped and are free to diffuse both towards the surface and deeper into the sample. In situations where the diffusion is being inhibited, such as in the case of the Alcator

Figure 4.16 The D depth profiles at the temperature steps for a thermal desorption after a Alcator C-Mod tile exposure with $T_{mo}=300$ K and $E_{D+}=30$ eV.

Figure 4.17 The D depth profiles at the temperature steps for a thermal desorption after a W lamellae exposure with $T_W=400$ K and $E_{D+}=30$ eV.

Figure 4.18 The fraction of the D content desorbed in a single spectrum time (250 s for 30 and 350 eV, 300 s for 100 eV) as a function of temperature for pure Mo plate at all ion energies.

C-Mod tile and the W lamellae, the behavior becomes more complicated. It will depend on what is causing the inhibition and if it is a global effect (such as the presence of a lamellae boundary) or a local effect (such as boron collected in the grain boundaries). The rate of desorption as a function of temperature can also yield information about the trap energies for the D traps. For the thermal desorption, because we only take a single spectrum at each temperature the total amount of D desorbed over the course of the spectrum time can not be measured. However, there are measurements of this type in the time after a plasma exposure when the specimen is kept at elevated temperatures. During this time, consecutive spectra are taken and as long as the spectra are taken at a long enough time after the plasma is turned off and the trapped and solute D are assumed to have come to equilibrium, these spectra can give a rough measurement of fraction of trapped D desorbed as a function of temperature and time. These values are given for the five exposure temperatures (300-700 K) for the three D⁺ ion energies (300, 100, and 350 eV) investigated for the pure Mo

plate in Fig. 4.18. The general trend agrees with observations from thermal desorptions, that the majority of the desorption occurs at temperatures $\gtrsim 600$ K (the non-zero desorption at 300 and 400 K is likely due to scatter in the spectra data in combination with strongly peaked D depth profiles at the surface). This data can yield trap energies when fit with a model for thermal desorption. This is investigated further in sec. 5.3.

4.4 Dynamic Retention characteristics of Mo

One of the aspects that makes DIONISOS a unique experiment is that it can measure the D content of the surface region during a plasma discharge. Measurements of what has been labeled the dynamic retention can give insights to how a PFC material can store plasma ions while being bombarded with a constant ion source. The retention rate as a function of time will determine if the retention is reaching saturation or equilibrium. This is one of the most important aspects of this study. The point at which the PFC saturates will be the key to determining the long-term retention characteristics for a PFC material in a long-pulse or steady-state fusion device and the feasibility of that material in a device using tritium as a plasma fuel.

4.4.1 Experimental Procedure

If it assumed that surface recombination is the limiting process in holding deuterium in the surface during a plasma exposure, then any drop in the D concentration in the surface layer immediately after the plasma is turned off can be attributed to surface recombination releasing solute but non-trapped D now that the plasma ion source has been removed. The basis for this method is conservation of flux illustrated by the equation:

$$\Gamma_{D+,IN} = \frac{1}{2}\Gamma_{D2,OUT} = \frac{1}{2}(\Delta n_D)^2 R \quad (4.1)$$

Where $\Gamma_{D+,IN}$ is the flux density of D+ ions into the target, $\Gamma_{D2,OUT}$ is the flux density of deuterium molecules out of the surface due to recombination, Δn_D is the change in deuterium concentration in the surface layer when the plasma is turned off, and R is the surface recombination coefficient at the target temperature. The plasma flux into the surface is well known from Langmuir probe

measurements and the value of Δn_D can be measured and the coefficient R can be solved. This method assumes that the surface has reached an equilibrium value during the plasma exposure and this is not the case for all of exposure conditions and temperatures but this method should still yield reasonable approximations for surface recombination values at all exposure temperatures. To ensure that the change in deuterium concentration in the surface layer due to surface recombination excludes any contributions from thermal desorption, the thermal desorption rate as measured at a time long after the plasma had been removed was subtracted from Δn_D .

4.4.2 IBA Data on Dynamic Retention

The dynamic retention as a function of time will give indications if a saturation level is being reached. The dynamic retention for the pure Mo plate, the Alcator C-Mod tile and the W lamellae are separated into room temperature (Fig. 4.19), intermediate temperatures (Fig. 4.20), and high temperatures (Fig. 4.21). At 300 K, the retention in the first 5 μm is known to be diffusion limited and the expected square root dependence of the retention is seen in the data. At 400 K, the retention rates are much closer to a linear dependence with time (or fluence). At 500 K, the retention is starting to turn over and it appears that an equilibrium is being approached at this temperature. At 600 K and 700 K, the retention in the first 5 μm has come to an approximate equilibrium for most conditions. However it must be noted that at elevated temperatures, specifically for the 350 eV ion energy exposures, the retention is actually decreasing with time. These behaviors will be discussed more in sec. 4.4.3.

The Alcator C-Mod tile has the dynamic retention behavior that resembles diffusion-limited retention. This is not unexpected since the depth profiles of the D concentration in the Alcator C-Mod tile shows the majority of the retention takes place in the 0.5 μm thick boron-rich surface layer with only a small amount of deuterium making it to the deeper traps. Even at high temperatures, the Alcator C-Mod dynamic retention continues with the same behavior, increasing retention in time when all other samples have reached an equilibrium value. This may be another consequence of the reduced diffusion in the Alcator C-Mod tile. With the lower diffusion rates, only a small fraction of the retention will be deeper than the NRA detection range, but the retention in the first

Figure 4.19 The D retention in the first 5 μm of the surface as a function of time for all ion energies for the Mo plate and the Alcator C-Mod tile at a specimen temperature of 300 K. The dashed line is to aid the eye.

5 μm will still be evolving. For the pure Mo plate, at high temperatures much of the retention is occurring beyond 5 μm and the evolution at those depths can not be monitored. This may be an indication that the saturation or equilibrium seen for the pure Mo plate at high temperatures is a local saturation and is influenced by the rate at which trapped D diffuses past the first 5 μm as well as the balance between trapping and de-trapping rates.

The values of Δn_D for the pure Mo plate and the Alcator C-Mod tile are listed in Table 4.4. Any data points that are left blank are because the value for Δn_D was zero. This can be expected for some experiments since the very small changes can be lost in the natural scatter of the data or by the ion beam shifting position slightly when the RF plasma is turned off. Using eq. 4.1, these are then translated into surface recombination coefficients and graphing these values as a function of $1/T$, an exponential temperature dependence for surface recombination is found (see Fig. 4.22). The surface recombination coefficient as a function of target temperature is listed in Table 4.5 for

Figure 4.20 The D retention as a function of time for all ion energies for the Mo plate, the Alcator C-Mod tile and the W lamellae at a specimen temperature of a) 400 K and b) 500 K. The dashed lines are to aid the eye.

Figure 4.21 The D retention as a function of time for all ion energies for the Mo plate and the Alcator C-Mod tile at a specimen temperature of a) 600 K and b) 700 K. The dashed lines are to aid the eye.

Temperature	30 eV Mo	100 eV Mo	350 eV Mo	30 eV C-Mod
300 K	5.13×10^{26} D/m ³	3.85×10^{26} D/m ³	2.56×10^{26} D/m ³	-
400 K	3.08×10^{26} D/m ³	2.88×10^{26} D/m ³	2.56×10^{26} D/m ³	-
500 K	-	6.41×10^{25} D/m ³	5.13×10^{25} D/m ³	6.41×10^{25} D/m ³
600 K	1.15×10^{26} D/m ³	4.49×10^{25} D/m ³	2.11×10^{25} D/m ³	3.20×10^{25} D/m ³
700 K	7.24×10^{25} D/m ³	2.76×10^{25} D/m ³	1.22×10^{25} D/m ³	6.41×10^{25} D/m ³

Table 4.4 Measured values of Δn_D used to calculate the surface recombination coefficients for the pure Mo plate and Alcator C-Mod tile.

the Mo plate and Alcator C-Mod tile. The measured Δn_D for W lamellae was zero, so no surface recombination coefficient could be derived.

4.4.3 Discussion

Two important observations can be made from the dynamic retention data. First, for the pure Mo plate, there is a clear dependence of surface recombination rate on plasma ion energy. Plasma exposures with 350 eV D⁺ ions demonstrated the highest recombination rate, followed by exposures with 100 eV ion energies, and exposures with 30 eV ion energies consistently had the lowest calculated surface recombination rate. Since the total D retention has been shown to have no dependence on ion energy it can be assumed that this energy dependence of surface recombination is

Specimen	Surface Recombination function [m ⁴ /s]
Mo Plate 30 eV	$5 \times 10^{-30} \exp(-0.18 \text{ eV/kT})$
Mo Plate 100 eV	$2 \times 10^{-28} \exp(-0.25 \text{ eV/kT})$
Mo Plate 350 eV	$8 \times 10^{-28} \exp(-0.28 \text{ eV/kT})$
Alcator C-Mod tile	$1 \times 10^{-30} \exp(-0.015 \text{ eV/kT})$

Table 4.5 Surface Recombination Coefficients as functions of temperature from fits to data in Fig. 4.22.

Figure 4.22 Surface Recombination Coefficients as a function of temperature for all ion energies for pure Mo.

not affected by the retention properties of the Mo. There is another effect that is strongly dependent on ion energy and that is the sputtering rate. It was stated in sec. 4.2.1 that for D⁺ energies of 350 eV, the sputtering yield of Mo was 0.002-0.006. This translates into 45-135 nm of Mo sputtered from the surface for a plasma fluence of 1.5×10^{24} D/m². For D⁺ energies of 30 eV, there is no sputtering since this value is below the energy threshold for sputtering of Mo by D. The 100 eV D⁺ ions are very close to the sputtering threshold energy [80] but have a sputtering yield of $\sim 1 \times 10^{-5}$. This translates to 1-2 nm of Mo sputtered from the surface. It was mentioned in sec. 1.2 that even a small amounts of surface oxides can reduce surface recombination rates [17, 19, 20]. Since the DIONISOS chamber can not achieve ultra-high vacuum levels (10^{-9} - 10^{-10} torr), it is likely that there is a thin oxide and impurity layer on the surface of the Mo. For the 30 eV plasma exposures, this oxide layer will be present through the entire exposure since the ion energy is below the sputtering threshold. However, for 100 eV and 350 eV ion energies, sputtering is taking place.

The lower sputtering rate of the 100 eV ion may be able to sputter away the thinner sections of the oxide layer but not the thicker sections meaning the recombination rate would be increased but not at its maximum value obtained with a pure Mo surface. The 350 eV sputtering yield of 45-135 nm is likely to have entirely sputtered away the oxide layer and so the surface recombination rate increases even more. This sputtering away of the oxide layer may also have some impact on the dynamic retention behaviors of the Mo.

The surface recombination rate of the Alcator C-Mod tile is difficult to resolve into a function of temperature since no Δn_D value was obtained for 300 K or 400 K. The surface recombination rates found for 500-700 K are scattered but yield a relatively flat profile when plotted versus temperature (see Fig. 4.22), which is very different from the functions found for the pure Mo specimen. This is not unexpected given the fact that there is a $\sim 12\%$ B impurity in the surface layer and it is clear that surface impurities can inhibit surface recombination. Since the Alcator C-Mod tile plasma exposures were performed with an ion energy of 30 eV, it can be assumed that no sputtering took place either of the Mo or permeated B.

The dynamic retentions of the specimens yield some very interesting results. For 300 K, the results are similar for all energies and specimens. At this temperature the D is diffusion limited and can not access the deeper traps. Diffusion limited processes are typically characterized by a square root dependence with fluence. This appears to be the case for the 300 K data. At 400 K, the depth profiles for pure Mo show that the D retention is no longer diffusion limited over the first 5 μm . Also, at 400 K we know thermal desorption is not a strong contributor to the overall retention behavior. This indicates that the thermal de-trapping rate is still low. This combination leads to a retention rate that is only limited by the availability of traps. If traps are being created at a constant rate by the plasma and the ion beam, this would lead to the linear of retention with time. The retention of the Alcator C-Mod tile and W lamellae specimens still display a square root dependence indicating that their retention is still diffusion limited. This is confirmed by the depth profiles.

At 500 K, the retention for pure Mo is not diffusion limited but it is still starting to turn over and appears to be approaching a saturation level. The 30 eV and 30 eV re-do exposures are approaching

different saturation levels despite having the same exposure conditions for the same specimen. It is possible that this is due to having more available trap sites due to previous irradiations. Saturation should be reached when the de-trapping rate is equal to the trapping rate. The de-trapping rate will be dependent on temperature and the number of filled traps. The trapping rate will depend on the mobility of D in Mo (also dependent on temperature) and the number of available/empty trap sites. If the thermal desorption does not anneal out all trap sites, then the 30 eV re-do exposure would have more available trap sites from the repeated irradiations than the original 30 eV exposure meaning the saturation level for that temperature will increase.

At 600 K, it appears that saturation levels have been reached for pure Mo and in the case of 100 eV and 350 eV exposures the retention appears to be decreasing in the first 5 μm of the surface at the end of the exposure. This decrease may have to do with changing surface recombination rates for these exposures. It was mentioned that the surface recombination will increase as surface oxide layers are sputtered away, so it is possible that the surface recombination is increasing with time for the 100 eV and 350 eV exposures. This increase in surface recombination will lead to a reduction in solute D, since surface recombination is likely the limiting process, and this reduction in solute D will lead to a reduction in trapping rate and a new saturation level. This also explains why the retention level for 30 eV exposures is higher than for 100 eV or 350 eV exposures at 600 K.

At 700 K, it again appears that saturation levels have been reached for pure Mo. The 350 eV exposure shows an initial rise in retention and then a very strong decrease over the course of the rest of the exposure. At this high temperature, the saturation level might be quite low, especially with the high recombination rate. The initial jump up in retention may be another indication of a history effect. Empty traps remaining from previous irradiations would allow the D to immediately find abundance of available traps. Then as the exposure progresses, the increase of the surface recombination as well as the erosion of the oxide layer, where the retention level may be locally high, contribute to the lowering of the saturation level. Because the retention levels are much lower at this temperature, effects that go unnoticed at lower temperatures, such as the removal of the oxide layer and the D retained within that layer, may play a more important role.

The dynamic retention data reveals important behaviors at various temperatures. It demonstrates how different the retention characteristics can be at temperatures only 100 K different. This understanding of dynamic behavior is the understanding that was missing from the field of plasma-surface interactions. The comparison of the dynamic retention of the Alcator C-Mod tile to the pure Mo plate specimens also shows how diffusion can play a role in determining local saturation or equilibrium retention levels. When looking at the first 5 μm of the surface, a higher diffusion rate will lead to a lower equilibrium value being reached more quickly in that local depth of the surface. This is due to the rate at which the trapped D being "lost" to the bulk of the material where it can no longer be measured and how that relates to the rate at which D is being implanted and trapped in the surface region. This is demonstrated by the Alcator C-Mod tile not reaching a retention equilibrium in the first 5 μm of the surface at high temperatures where the pure Mo plate has established an equilibrium.

4.5 Effects of Dynamic Specimen Temperature

In most current tokamaks, including Alcator C-Mod, the wall tiles are not actively cooled. Instead, they are inertially cooled by ensuring the wall tiles are in good thermal contact with the vacuum vessel. Even for short plasma discharges, the divertor can experience heat loads as high as $\sim 10 \text{ MW/m}^2$ in Alcator C-Mod and this can increase the wall temperature to $\sim 1200 \text{ K}$ in a matter of seconds. Since there is no temperature control and the wall heating is from plasma loading, the wall temperature is increasing with time due to the heat load from the plasma. The previous sections have already shown how the retention behavior can change significantly with temperature, so to understand retention behaviors in current tokamaks, the effects of dynamically increasing temperature must be investigated.

4.5.1 Experimental Procedure and Exposure Conditions

The helicon source in DIONISOS can not produce plasma flux densities high enough to provide enough heat flux to the target to provide significant heating. Instead, the entire specimen is heated with the temperature control available on the DIONISOS sample holder. A constant DC current is

passed through the cartridge heaters on the sample holder. This provides a constant heat load to the target similar to what is provided by the plasma in a tokamak experiment, although, in a tokamak, the heat load is provided through the surface of the target instead of the backside as in DIONISOS.

This method provides a near-linear temperature ramp from 300-600 K in the 1500 s plasma exposure. Once the plasma is turned off, the active heating is also turned off and the specimen is then actively cooled to reduce the temperature back to ~ 300 K in under 300 s. This cooling simulates what is experienced by the wall tiles in a tokamak that are in good thermal contact with a large temperature sink at 300 K.

NRA is used to monitor the D retention throughout the exposure and the exposure procedure and experimental conditions were the same as those used in the steady-state temperature exposures (see sec. 4.2.1). Dynamic temperature exposures were performed on pure Mo plate from Batch A at ion energies of 30, 100, and 350 eV.

4.5.2 IBA Data for Plasma Exposures with Dynamic Specimen Temperature

Fig. 4.23 shows the dynamic D retention in the first 5 μm of pure Mo for plasma exposures with increasing specimen temperature and ion energies of 30, 100, and 350 eV. The data shows that ion energy has little effect on the dynamic retention in this case. This is not surprising since the temperature is only ramped up to ~ 600 K and from Figs. 4.4, 4.19, and 4.20 we know that the retention is approximately the same for all ion energies at temperatures < 700 K. The dynamic retention does give some insight to how the retention behavior can change rapidly with changing temperature. The data shows an initial jump in the data followed by a slow rise in retention until about 1000 s at which point the retention decreases with time until the end of the plasma exposure. When the plasma is turned off there is a large drop in the overall retention, which can be expected for surface recombination limited retention but it is surprising that the 350 eV data displays such a large drop when plasma exposures at these ion energies were measured to have the largest surface recombination rate. This may also be an effect from the rapidly decreasing temperature for the time at which this spectrum was being obtained. After this initial drop from the removal of the

plasma, the retention levels for the 30 eV and 350 eV cases show a small rise in D content even though the Mo is at room temperature.

More interesting is how the depth profiles of the D concentration in the surface evolve with a dynamically changing temperature (see Figs. 4.24-4.26). Initially the D retention is isolated to the surface as is expected when the temperature is <400 K. As the temperature increases, the D that was trapped at the surface now has access to the deeper traps in the surface and begins to diffuse into the Mo. This process continues but the retention levels begin to decrease, although as seen from the flat D/Mo profiles deep into the sample, this is an artifact of only being able to account for D in the top $5\text{ }\mu\text{m}$. The depth profile continues to flatten as the temperature continues to rise throughout the plasma exposure. After the plasma is turned off, it appears that the increase in D content seen for the 30 eV and 350 eV cases is due to D migrating back to the near surface. This D migrating back to the surface is likely to originate from deeper in the sample, implying the presence of D past the detection range.

4.5.3 Discussion

The dynamically changing specimen temperature had a strong influence on the retention behavior of the Mo. By ramping the temperature up from 300 K to 600 K, the retention behavior goes through three distinct changes. First as the temperature ramps from 300 K to 400 K, the D is implanted in large quantities but diffusion limited to the near surface. As the temperature ramps from 400 K to 500 K, the D gains access to the deeper traps and overall retention increases and the D concentration depth profile extends beyond the near surface. From Fig. 4.4 we know that the retention levels decrease between 500 K and 600 K, likely due to thermal de-trapping playing a larger role at these higher temperatures. This is seen in the current data as well (see Fig. 4.23) where the retention begins decreasing after 1000 s into the run. At this time, the Mo temperature is ~ 490 K and still increasing. The retention continues to decrease as the temperature increases up to ~ 600 K.

A drop in retention once the plasma is turned off is expected, but the magnitude of the drop in this case is surprising. In the case of the 350 eV exposure, the retention drops by $\sim 50\%$ when the

Figure 4.23 The D retention for pure Mo as a function of time for a plasma exposure with a dynamically increasing specimen temperature.

Figure 4.24 The D concentration depth profiles for dynamically changing temperature with plasma ion energy of 30 eV. The solid lines are during the plasma exposure and the dashed lines are after the plasma exposure. The times correspond to the x-axis in Fig. 4.23.

Figure 4.25 The D concentration depth profiles for dynamically changing temperature with plasma ion energy of 100 eV. The solid lines are during the plasma exposure and the dashed lines are after the plasma exposure. The times correspond to the x-axis in Fig. 4.23.

Figure 4.26 The D concentration depth profiles for dynamically changing temperature with plasma ion energy of 350 eV. The solid lines are during the plasma exposure and the dashed lines are after the plasma exposure. The times correspond to the x-axis in Fig. 4.23.

plasma is turned off. It is not likely that a change this large could be due to surface recombination effects. The rapidly decreasing temperature when the first spectrum after the plasma exposure was taken could be playing an important role, but from the data available, the physics behind this effect are not clear.

The retention levels at the end of the exposure are also quite low when compared to the values seen in Fig. 4.4. For the dynamically changing temperature the D retention levels at the end of the plasma exposure were all $\sim 2 \times 10^{20}$ D/m². This is an order of magnitude lower than the retention seen at 400 K and 500 K steady-state plasma exposures and a factor of 3-6 lower than for 300 K and 600 K steady-state plasma exposures. It is possible this is somewhat due to a history effect since the higher temperature data in Fig. 4.4 was taken after repeated irradiations and thermal cycles. This is quite a large difference to be made up for by a history effect. Another factor may be that the retention level is controlled by the last temperature with the plasma present. So even though retention was expected to be much higher for 400 K and 500 K, because it quickly transitioned into the higher temperature range the retention did not have a chance to accumulate at the lower temperatures where retention rates are higher.

Another important effect of the temperature ramping and rapid cooling is the "locking" of deuterium deep in the target. After the rapid cooling there is still deuterium trapped to the extent of the detection range and because the specimen is now back at room temperature, thermal detrapping and deuterium and trap mobility will be very low. If this thermal cycling was repeated it would have a "ratchet" effect on the depth of the deuterium. When the temperature is raised again the D is free to move even deeper into the bulk and is now locked in at its new depth when the rapid cooling occurs. This effect is somewhat contradicted by the 30 eV and 350 eV data that show D returning to the surface after the plasma has been turned off. It is not clear how the D appears to stay mobile at those low temperatures. The cause for the D moving back to the surface is thought to be because of the large drop in the D retention for these two ion energies when the plasma was turned off. This large and relatively sudden drop in D content in the first 5 μm of the surface may induce some D from depths of $>5 \mu\text{m}$ to return to the surface region. This would also explain why this effect was not seen as clearly for the 100 eV case.

Overall, it is clear that dynamically changing surface temperatures can have complicated effects on retention due to competing processes with exponential sensitivity to temperature. This complexity becomes a strong motivation for the application of numerical simulations in Chapter 5, in which one can keep track of these dependencies.

4.6 Surface Effects and Impurities

It was mentioned in sec. 2.3 that it is unclear what effects surface blistering and void formation can have on trapping. Some theories predict bubble formation in metals can provide non-saturable traps which would have a serious impact on retention. However, retention studies have shown no direct correlation between the formation of visible surface blisters and an increase in retention. In DIONISOS, the high flux, low energy plasma combined with the low solubility of D in Mo is a recipe for bubble formation according to Condon et al [5]. Irradiation can also form voids in the metal but temperatures >900 K are required for vacancy clusters to coarsen into voids [66, 71]. Since these temperatures are not obtainable on DIONISOS it is unlikely that the ion beam irradiation will lead to the formation of bubbles or blisters. To confirm if surface blister formation is taking place in DIONISOS, several specimens were examined with SEM and Zygo Interferometry for blisters $\gtrsim 0.5$ μm in diameter.

It is also known that surface impurities can play a strong role in determining surface recombination rates [17, 19, 20] and impurities can also reduce the diffusion rate of hydrogenic species in Mo [41, 6]. Impurities could be introduced to the Mo either through surface oxidation or by deposition of plasma impurities. Impurities in the surface region are measured with ion beam analysis and XPS.

4.6.1 Ion Beam Analysis

Since energetic ^3He undergoes nuclear reactions with several different elements, ^3He NRA is a useful tool to check the near-surface region for impurities. There are nuclear reactions between ^3He and carbon and oxygen, which are two of the most common vacuum and plasma impurities. Since the reaction products for both carbon and oxygen are protons of similar energy it is possible to

measure both C and O content of the surface region in a single spectrum. The ^3He NRA spectrum is shown for the Mo plate used for the 30 eV plasma exposures from a point in the center of the plasma column (Fig. 4.27a) and a ~ 1 cm off center (Fig. 4.27b). In both spectra there are clear C peaks and a low energy peak that may be from oxygen. The carbon peaks are very narrow indicating only a thin layer of carbon on the surface. Since the depth resolution for this NRA is only 250 nm we know the C is at a depth of <250 nm. The simNRA fit can either be for a small amount (0.1 %) of C spread across the entire 250 nm or higher concentrations but in a thinner layer. The oxygen peak does not fit as well as the carbon peaks. Since the peak occurs at such low energy it is often difficult to obtain an accurate energy calibration for the low energies. This would explain why the peak appears to be shifted to lower channels in the simNRA fit. Also the magnitude of the peak is much too low in the fit. This may be due to the peak in the data resting on top of a low energy tail. Low energy noise is often a problem with solid state detectors and this may be causing the oxygen peak to be so poorly fit. Since ^3He is so reactive and there are numerous high energy protons produce from the reactions with D, C, and O, there are also several other peaks seen in the spectra. One possibility for these additional peaks is nitrogen. Since all peaks observed are narrow, it is likely that they all originate from the very near surface.

In that same spectrum there is also a peak that represents the D content. This peak is from the energy lost by the protons created in the $^3\text{He}(d,p)\alpha$ reaction as they pass through the detector. Since the energy of these protons can not be fully absorbed by the depletion depth of the detector, this is not a true detection peak but what is called a depletion peak. Depletion peaks can not be fit in simNRA. One interesting point is that the carbon and oxygen peaks do not correlate with the amount of D in the surface. Since the D content can be directly related to the local plasma fluence, this is a strong indication that these C and O impurities are not originating from plasma deposition and do not have a direct correlation with D retention.

4.6.2 XPS

Since it is suspected that the impurities are concentrated at the surface, XPS seemed the best-suited surface diagnostic for our needs. XPS provides an elemental and chemical composition

Figure 4.27 The ^3He NRA spectra showing the carbon, oxygen, and deuterium depletion peaks for a point a) in the center of the plasma column, and b) ~ 1 cm off-center.

Element	Specimen A	Specimen B	Specimen C	Specimen D
Mo	16.7 %	3.5 %	4.6 %	9.4 %
C	36.6 %	65.6 %	34.3 %	36.4 %
O	31.5 %	21.5 %	17.5 %	19.0 %
Si	15.2 %	9.5 %	41 %	35.1 %
Fe	-	-	2.3 %	-
Total	100 %	100 %	100 %	99.9 %

Table 4.6 The elemental composition of the Mo surface as measured by XPS.

of the first 2-3 nm of the surface. Four samples, A, B, C, and D, were examined with XPS. All of these samples were from Mo Batch B (see Tab. 3.2). Since the samples were too large to be inserted into the XPS chamber, they had to be cut into smaller pieces. Extra care was taken not to disturb the surface during machining.

Specimen A was kept in the "as received" condition. This specimen had never been put into vacuum, baked, or exposed to a plasma or ion beam. Specimen B was exposed to a 30 eV plasma at a temperature of 300 K for 60 minutes with no ion beam present. The Langmuir probe was inserted into the edge of the plasma throughout the exposure. This specimen is intended to check for deposition at low temperature and to check for impurities introduced through the Langmuir probe interaction with the plasma. Specimen C was exposed to a 30 eV plasma at a temperature of 500 K for 1500 s with the ion beam present. The Langmuir probe was not inserted during this plasma exposure. This specimen was intended to check for higher temperature impurity deposition and also to provide an approximate reference for specimen B and the check for contributions from the Langmuir probe. Specimen D was taken from the back side of specimen C. This specimen underwent all the same thermal cycling and vacuum conditions as specimen C but was never exposed to the plasma. This is another check for plasma deposited impurities. The results show the surface of all specimens to be composed of four elements: Mo, C, O, and Si (there was also a small amount of Fe detected on specimen C). The exact elemental compositions can be seen in Table 4.6.

Some other elements that were looked for but not found were Ni, Cr (from the Nichrome wire used for the Langmuir probe), Al, Zr (Alumina from the Langmuir probe ceramic), Cu (from the heat sink), and B. Only a small fraction of the surface is Mo with the majority of the layer consisting of C and Si. Carbon is not unexpected as it is a common vacuum and atmosphere impurity and could be absorbed into the surface and its presence was measured by NRA as well. The oxygen is also expected to be present from NRA. The source of the silicon is not known for certain although it likely does not originate from the DIONISOS system since it was already present in specimen A. When this Mo is fabricated, the surface finishing is done with glass (SiO_2) beads. It is possible that the silicon was ingrained into the surface during this process. Seeing how similar Specimen C and D are, it is unlikely the plasma has any effect on the surface impurities, at least for a specimen temperature of 500 K. The higher carbon content for specimen B is not easily explained. The lower Si might be due to the Si being covered up by the C. This would imply a deposition process. It is possible that the Langmuir probe is somehow contributing carbon impurities to the plasma but it is not clear how since carbon is not one of the materials used in the construction of the probe. Perhaps it has nothing to do with the probe but instead the deposition is possible because the specimen temperature was kept at 300 K.

If an average carbon concentration of $\sim 40\%$ is assumed and this value is used in the fit for the NRA data, this translates to a 40% carbon layer that is ~ 10 nm thick. The layer would be slightly thicker or thinner depending on the exact carbon concentration but it is clear that these impurities are concentrated in a thin layer on the surface of the Mo. Since this layer is so thin, it is unlikely that it will contribute significantly to the total D retention of the Mo, but since the implantation range for the D ions is so small (2-10 nm) it is possible that this impurity layer could affect the diffusion of D near the surface and will certainly affect the surface recombination. However, it should be noted that the exposure conditions and vacuum quality of DIONISOS are typical of what will be found in a fusion experiment.

Figure 4.28 Zygo Interferometry images.

4.6.3 SEM and Zygo Interferometry

Since there is no in-situ SEM or surface magnification devices on DIONISOS, it is difficult to monitor the surface for blistering after all exposures. The Mo plates that were used for the 30 eV, 100 eV, and 350 eV were checked for surface blistering after the data was taken for all temperatures. Due to the large surface area of the Mo plates, examination under SEM would be cumbersome and time consuming. The Mo plates were first examined with a Zygo Interferometer. The interferometer can operate in air making it much more user-friendly than a SEM, especially when dealing with large samples. The vertical resolution of the interferometer is $<1\ \mu\text{m}$ but the horizontal resolution is only $\sim 10\ \mu\text{m}$. This means only large surface blisters will be detectable.

The results were that no blistering was observed on the 30 eV or 100 eV plates but there was some very large surface blister formation on the 350 eV plate. The blistering was not centered on the plasma column. The blistering was concentrated in a $\sim 1.5\ \text{cm}$ diameter spot that was $\sim 2\ \text{cm}$ to the right of the plasma column. It is not clear why the blistering is concentrated in this region since any point off the center of the plasma column is likely to have a reduced plasma flux density making it less susceptible to blistering. In any event, the blisters were measured to be quite large, some as big as $\sim 60\ \mu\text{m}$ in diameter (see Fig. 4.28b). The blisters are $\sim 3\ \mu\text{m}$ in height and the surface roughness characteristics can be seen on the top of the blister, indicating that the blister is formed from deeper in the sample (see Fig. 4.28a). The blisters do not cover the entire area but they are reasonably closely packed (see Fig. 4.28c). Despite the presence of these large blisters, it has little effect on the total retention since the retention has been shown to have little dependence on ion energy. It may be that there is blistering present for the other ion energy plasma exposures but the blister size is smaller than the Interferometer spatial resolution. So instead of large blisters, there could be smaller blisters in higher number densities. To investigate this, several samples of the Mo foil (see sec. 3.3) were exposed to a variety of plasma exposures at different temperatures. Two specimens were exposed to 100 eV ion energy plasmas at temperatures of 300 K and 600 K. One specimen was exposed to 30 eV ion energy plasma at a temperature of 500 K. The SEM shows no blister formation for the 30 eV/500 K exposure or the 100 eV/600 K exposure. On the 100 eV/300 K specimen there was a small cluster of blisters found. These blisters were 50-100 nm

Figure 4.29 Nanometer scale blisters in a small μm -scale cluster on the surface of Mo foil that was exposed to a 100 eV plasma at 300 K.

in diameter but were only found in a cluster in a spot only $\sim 3 \mu\text{m}$ in diameter. No other clusters like this could be found on the surface. Blister formation that is this localized could not contribute significantly to retention characteristics.

Since significant blistering is only seen for 350 eV ion energy plasma exposures but the retention was found not to depend on ion energy, the conclusion can be made that surface blistering does not affect deuterium retention in the DIONISOS exposures.

Chapter 5

Modeling

There is an abundance of experimental results in this study. From these results, many conclusions about the hydrogenic retention behaviors of Mo can be made. However, conclusions must be based on well-known physics. If the physics behind the processes have been well-defined then a simulation should be able to re-create the experimental results. Such a simulation was created to test some of the conclusions reached based on the DIONISOS experimental data.

Also, due to the complexity of the hydrogenic retention in DIONISOS, including all the complications from ion beam damage, surface impurities, temperature history, etc, a simple extrapolation from the DIONISOS experiment to the tokamak situation impractical. However, using the unambiguous measurements of the depth profiles of the D as a function of time, temperature and exposure in DIONISOS, a well-founded model can more easily extrapolate to the tokamak situation for current experiments and future devices.

5.1 Model Structure and Assumptions

The simulation consists of two parts. There is an input file that provides all the values used to calculate rates such as diffusion, surface recombination and thermal de-trapping and also defines exposure details such as trap production rate, plasma flux density and specimen temperature. These inputs are used in a model that then simulates a plasma exposure and irradiation of the surface. Since the physics behind the dynamics of plasma-surface interactions has been so poorly diagnosed in the past, there is very limited understanding on which to base the model. Because of this and to keep the model simple and efficient, some assumptions were made. Most assumptions are

justified in the following sections by showing they improve the fit to the experimental data and some assumptions are based on physics arguments.

There are two key assumptions that are made strictly for the sake of simplicity. It is assumed that there is only a single type of trap present in the target. This implies that there is only a single diffusion rate for traps. The literature states that this is likely not the case and that in irradiated samples there is likely a mix of vacancies, vacancy clusters and dislocations formed and it is likely that all these traps will have different diffusion rates through the target and different trap energies. One type of trap is assumed because there is limited or no data available for the diffusion rates of the different trap types, the relative quantity of one trap type to another and how these values change with substrate temperature. So, if the model allows for different species of traps, this will lead to even more assumptions about how these different trap types behave. The second key assumption is that each trap can only hold a single D atom. Again the literature states that in some materials even vacancies can hold more than a single hydrogen atom [81] and it is likely that vacancy clusters and voids could also hold more than a single atom. However, due to a lack of information about the behavior of a partially filled trap compared to a fully filled trap, it is safer to assume a single D atom for each trap site.

The simulation is a 1-D numerical slab model based on flux conservation written in the MATLAB language. Details on the flux and particle conservation equations and how they are solved can be found in Appendix A. One of the most difficult challenges in using a numerical model to recreate the DIONISOS experimental data is keeping the model numerically stable. The plasma exposure is on a long time scale (1000-1500 s) but the data is acquired across a very thin layer (5 μm). For a model that relies heavily on particle diffusion and density gradients, the time steps must scale like the square of the slab thickness to keep the code numerically stable. Again, since we are dealing with long time scales and small slab thicknesses this can make the code computationally cumbersome. The depth resolution is limited by the smallest time step that is achievable without running into memory limits on the computer. The final configuration that was stable up to 700 K was a time step of 0.003 s and a slab thickness of 1 μm . There are 10-20 slabs in total meaning the

simulation tracks retention over the first 10-20 μm of the surface. Twenty slabs is the maximum number of slabs before memory limitations are encountered.

An example of a typical input file can be found in Appendix B. Some values entered, such as diffusion rates, trap production efficiencies, and thermal de-trapping in this file are deduced by fitting to the experimental results and these will be explained further in the following sections. Other values, such as surface recombination rates and the damage depth distribution from irradiation are taken directly from DIONISOS results and TRIM calculations. There are some values that are based on a physics basis to the best of our knowledge. One of these values is the plasma flux density. The incident plasma flux density is well known from the Langmuir probe measurements, but the model needs to account for particle reflection from the surface. A reflection model for light ions has been published by Eckstein [82] in which particle reflection coefficients can be calculated for any incident ion onto any substrate using equations from Ito et al [83]. For deuterium ions ranging in energy from 30 eV to 350 eV, the reflection coefficient was found to be within 10% of 0.5 for all energies. So, in the simulation, it is assumed that 50% of the incident plasma flux will reflect from the surface and the other 50% will be implanted in the material.

Another important factor that is based on physics arguments is the rate coefficient at which solute deuterium will occupy available trap sites. A rate coefficient in its standard form is a cross-section multiplied by a velocity, $\langle\sigma v\rangle$. The cross-section in this case is assumed to be the cross-section of the trap site energy well. It is assumed this relates closely to the physical size of a vacancy, which is assumed to be approximately the size of an atom. If this is assumed to be roughly spherical with a radius of 3-5 angstroms, this corresponds to a cross section of $\sim 1 \times 10^{-19} \text{ m}^2$. The velocity term is taken to depend on the diffusion of solute D and the length of each time-step. For a random walk diffusion process, a hydrogen will travel outwards from a point to a mean-square radius of $6Dt$, where D is the diffusion rate and t is the time of travel [84]. To translate this mean-square radius into a relative velocity, we take the square root and divide by time. A factor of two is added for normalization and the resulting velocity is:

$$v_r = \sqrt{\frac{3D}{2t}} \quad (5.1)$$

This equation is found in the model file, not in the input file since the diffusion rate must first be calculated. Combining the cross-section and the relative velocity terms, a rate coefficient is obtained:

$$\langle \sigma v \rangle_r = 1 \times 10^{-19} [m^2] \cdot \sqrt{\frac{3D}{2t}} [m/s] \quad (5.2)$$

The thermal detrapping rate is fit with experimental data from sec. 4.3 on heating removal of the D. We fit the process as an Arrhenius relationship. These are expected for thermally-driven processes and feature a generic form of "rate constant" $\times \exp(-E_{act} / kT)$. The rate constant and E_{act} , the activation energy, can in principle both be fit from experimental data. If the coefficient in front of the exponential can be reasonably approximated, this allows the fit to the experimental data to determine the trap energy (i.e. E_{act} for thermal de-trapping). The coefficient should have units of 1/s to define a rate. It is assumed the this rate would be the number of "attempts" to escape the energy well per second. This number would be equal to the oscillation frequency of the D atom in the trap. If the trap is assumed to be ~ 1 nm wide and the D atom is traveling at 2000-3000 m/s, this translates into a coefficient of $1 \times 10^{12} \text{ s}^{-1}$.

Trap annealing is another process that is difficult to quantify. It is clear that annealing at high temperatures can remove trap sites from a surface and that this is likely a process that is exponentially dependent on temperature much like surface recombination for D release. It is not possible to directly measure the trap densities themselves since NRA can not detect empty trap sites. Rather we can infer trap densities indirectly from the static D profiles measured with NRA. As the traps are annealing the trapped D is also being thermally desorbed leaving behind empty trap sites that NRA can not detect. The best measurement of trap annealing is based on the bake times required to remove 90+% of the D in the surface. It is assumed that when all D is removed from the surface that all traps are also annealed, a suspect assumption considering the data suggesting a history effect from irradiations. However, this is not thought to be a dominant effect since retention in subsequent experiments does not immediately return to previous values. We know for a bake temperature of 720 K takes ~ 60 minutes to removed all the D from an exposure at 400 K. We can approximate an annealing rate for this temperature but we also have to assume a activation energy for this exponential process. An activation energy of 0.5 eV is chosen. This is based on the

square root of a typical surface recombination activation energy measured in sec. 4.4. The square root is taken because it is assumed that trap annealing is solitary process that only depends on the trap density on the surface, where as surface recombination is a binary process that depends on the square of the solute D concentration at the surface.

An example of the simulation code can be found in Appendix C. This model is a flux conservation model but it also has the capability for heat conduction modeling. The model runs in a basic loop structure. It initializes the surface and conditions. Then it calculates the temperature and calculates the source and sink terms for the first slab. It cycles through all the slabs in this manner. When all source and sink terms are calculated for all the slabs, the time is stepped forward and the process is repeated, forwarding the results as necessary to the next time step for rate calculations. The boundary condition given to the final slab is an important factor to consider. In this model, the trap and D densities are set to zero in the final slab. This causes the final layer, which represents the rest of the "bulk" of the material, to behave as an infinite particle sink. This resembles what will happen for a PFC tile with a macroscopic thickness of ~ 1 cm. It also resembles what occurs in the DIONISOS NRA data where D travels down past the detection range and is no longer accounted for in the spectra. It is important to have this artificial boundary condition far enough away from the surface that its effects on the depth profiles for the first $5 \mu\text{m}$ of the surface are minimized. For 300 K, because the retention is diffusion limited, only ten slabs are required. For 400 K and 500 K, the number of slabs increase to fifteen, and for 600 K and 700 K the maximum number of slabs, twenty, is used. There are also several assumptions made in the model about damage distributions, specifically how they translate into traps and surface effects. These are discussed and rationalized in the following sections.

5.2 Fitting Deuterium Retention as a function of Surface Temperature and Plasma Ion Energy

The model needs experimental data to determine specific values for quantities such as diffusion rates and trap production rates and also to ensure that the physics behind the model are working properly. The most relevant data in this case is the retention data as a function of temperature. By

fitting the depth profiles for all temperatures and ion energies, this will likely result in a diffusion rate that is close to the actual rate and magnitude of the retention can then be fit by scaling the trap production coefficients.

The surface recombination rates are taken from the experimental data from DIONISOS. The initial diffusion rate of D in solution (i.e. solute D) is taken from Tanabe [35] with an activation energy of 0.55 eV. It was initially found that if a linear dependence between the irradiation damage and trap production was assumed, the simulation produced a rise in the D concentration at a depth of 4-5 μm for the depth profiles at 400 K and 500 K. This depth corresponds to the maximum damage from the irradiation. Since the experimental data shows a steady decrease in concentration from the surface to the end of detection range, a linear dependence between irradiation damage and trap production does not fit the data well. The experimental data showed that square root and 1/4-power dependences on dpa-to-trap conversions also provided acceptable fits (see sec 4.1.2). The 1/4-power dependence displays the best agreement between the data and the model and this distribution is assumed for the rest of the modeling. This dependence is of critical importance for nuclear damage estimates for fusion reactors. More data concentrating on this relationship is required and should be prioritized for future work. To best match the depth profiles for all temperatures an activation energy for solute D diffusion higher than Tanabe's value of 0.55 eV was required. Fig. 5.1 shows the effects of changes in diffusion rates for the solute deuterium. The best fit is a diffusion rate of $D_D[\text{m}^2/\text{s}] = 4 \times 10^{-6}[\text{m}^2/\text{s}] \times \exp[-0.66 \text{ eV}/kT]$ for the solute D and $D_{tr}[\text{m}^2/\text{s}] = 1 \times 10^{-8}[\text{m}^2/\text{s}] \times \exp[-0.55 \text{ eV}/kT]$ for the traps and trapped D. Note that empty and occupied traps are assumed to diffuse at the same rate, therefore trapped D is allowed to migrate in the material, albeit at a significantly reduced rate than solute D. It is not unreasonable to assume the trapped D is mobile since it has been suggested that hydrogen trapped in a dislocation can actually diffuse through a substrate faster than solute hydrogen [10, 65]. The concept of mobile trapped D is supported by simulations assuming mobile trapped D and immobile ("frozen") trapped D for the diffusion rates listed above show improved agreement to experimental results (see Fig. 5.2). The trap diffusion was chosen to be loosely based on the work of Naidu et al [71] who demonstrated

Figure 5.1 Comparison of various solute deuterium diffusion rates to 400 K data from 30 eV plasma exposures. The fits are labeled by diffusion activation energies.

Figure 5.2 Comparison of simulations assuming immobile trapped D ("frozen") and mobile trapped D to 400 K data at 30 eV plasma ion energies.

Figure 5.3 Diffusion rates for the bulk and surface layer of a pure Mo plate that yield the best fits to experimental data.

the diffusion of traps became significant at ~ 450 K. The trap diffusion is approximately two orders of magnitude lower than solute D diffusion for all temperatures examined in this study.

Work by Noda et al [41], shows atomic concentrations of $\sim 1\%$ of C and B distributed evenly throughout the material, can reduce the diffusion of solute D in Mo by an order of magnitude at low temperatures, but the reduction is smaller (factor of 2-3) at $\gtrsim 800$ K. Data from XPS and IBA show the Mo plate in DIONISOS, has much higher concentration of impurities at the surface but they are concentrated in a layer ~ 10 nm thick. Distributing this 10 nm layer across the first micron of the surface will result in a atomic impurity concentration of $\sim 1\%$. The model assumes a reduced diffusion rate for both traps and solute D in the first layer. The magnitude of the reduced diffusion rate is based on the observations from Noda et al. The lower diffusion rate at the surface increases the surface concentration of D in the simulation. However, it also affects the depth profile past the first layer of the Mo target. It is found that the diffusion of the bulk needs to be increased to compensate for the much reduced diffusion at the surface. Final diffusion rates that best fit the

experimental data were found to be:

$$\text{Solute D diffusion in bulk: } D_D[m^2/s] = 4 \times 10^{-6}[m^2/s] \exp[-0.63eV/kT] \quad (5.3)$$

$$\text{Trap/trapped D diffusion in bulk: } D_{tr}[m^2/s] = 1 \times 10^{-8}[m^2/s] \exp[-0.55eV/kT] \quad (5.4)$$

$$\text{Solute D diffusion in surface: } D_{D,surf}[m^2/s] = 4 \times 10^{-6}[m^2/s] \exp[-0.63eV/kT] \quad (5.5)$$

$$\text{Trap/trapped D diffusion in surface: } D_{tr,surf}[m^2/s] = 4 \times 10^{-6}[m^2/s] \exp[-0.63eV/kT] \quad (5.6)$$

These rates are plotted as a function of temperature in Fig. 5.3.

The shapes of the density depth profiles are recreated using these diffusion rates but the trap production rates must be scaled to fit the magnitudes of the D/Mo depth profiles. The data on the trap production rates shows that the plasma is responsible for 10-20% of the traps produced (see sec. 4.1.1) and that the beam-produced traps scale as $\text{dpa}^{1/4}$ (see sec. 4.1.2). Using this information, the trap production rates for the irradiation and the plasma have a set ratio. It is found that the plasma trap production rate coefficient is 7×10^{-4} and the irradiation trap production coefficient is 1.5×10^{-4} . Note that the plasma trap production rate is a function of incident D+ plasma ion and the irradiation trap production rate is a function of dpa. With these fixed relative production rates of traps, the retention magnitudes in the first $5 \mu\text{m}$ were matched for all temperatures. The simulation now reproduces the depth profiles for the 30 eV ion energy plasma exposures (see Fig. 5.4). The 350 eV ion energy plasma exposure situation also needs to account for any effects from the physical sputtering of the surface. It was hypothesized in sec. 4.4.3 that many of the differences seen in the 350 eV exposures as compared to the other ion energies, such as higher surface recombination coefficient and decreasing dynamic retention at high temperatures, could be explained by the sputtering of the oxide and impurity layer on the surface of the Mo plate. In the model, this impurity surface layer is represented by a surface layer of lower diffusion rates caused by the presence of low-Z impurities. Figs. 5.5 and 5.6 shows the comparison of the reproduction of the 350 eV experimental results with and without the reduced diffusion surface layer in the simulation. The reproduction without the reduced diffusion in the surface layer appears to more accurately reproduce the experimental results, particularly at 400 K, indicating surface erosion is removing the surface impurity layer and playing a significant role in retention behavior.

Figure 5.4 Comparison between the experimental data and numerical reproduction for 30 eV/D+ plasma exposures on pure Mo plate.

The 100 eV plasma exposure is also under different circumstances. Recall that the irradiation fluence for these exposures was lower but the plasma flux density was 50% higher (See Table 4.3). The lower irradiation fluence will mean fewer beam-produced traps but the higher plasma flux density will produce more plasma-produced traps. Since the experimental results show the total retention in the first 5 μm is approximately the same for all ion energies, it was inferred that the increase in plasma flux density must be compensating for the decrease in irradiation fluence. A pressure-driven plasma trap production mechanism was proposed. A mechanism based on pressure would scale linearly with the plasma flux density, since it is related to the implanted D density resulting from the flux exposure at constant temperature, and this is how it is written into the model. Fig. 5.7 shows that the agreement between simulation and experimental results is strong. This is excellent validation for a pressure-based trap mechanism for plasma-produced trap sites.

The Alcator C-Mod tile is much more difficult to model. The indications from the experimental data are that the boron-rich surface layer inhibits diffusion. The results also show a strongly-trapped inventory of D in this boron layer that can not be thermally desorbed in DIONISOS. The lower diffusion in the surface layer can be accounted for in the model but the strongly trapped D can not be easily added to the code since it is assumed there is only a single trap type. Working

(a) 300 K and 400 K

(b) 500 K, 600 K, and 700 K

Figure 5.5 Comparison between the experimental data and numerical reproduction for 350 eV/D+ plasma exposures on pure Mo plate with reduced diffusion in the surface layer.

(a) 300 K and 400 K

(b) 500 K, 600 K, and 700 K

Figure 5.6 Comparison between the experimental data and numerical reproduction for 100 eV/D+ plasma exposures on pure Mo plate without reduced diffusion in the surface layer.

Figure 5.7 Comparison between the experimental data and numerical reproduction for 100 eV/D+ plasma exposures on pure Mo plate.

with the assumptions made in the model, the best fit surface diffusion rates for solute D and traps are:

$$\text{Solute D diffusion in surface: } D_{D,surf}[m^2/s] = 8 \times 10^{-11}[m^2/s] \exp[-0.4eV/kT] \quad (5.7)$$

$$\text{Trap/trapped D diffusion in surface: } D_D[m^2/s] = 1 \times 10^{-8}[m^2/s] \exp[-0.8eV/kT] \quad (5.8)$$

The experimental results also showed the surface recombination rate for the Alcator C-Mod tile to be very different than for the pure Mo plate (see Table 4.5). However, this result is somewhat weak since the fit was only made for 3 data points with large scatter. For higher temperatures, the surface recombination rate is similar to that obtained for 100 eV plasma exposures, but there is a large difference for the 300 K and 400 K cases. The fit to the experimental data is found to be better if the 100 eV surface recombination rate is assumed. The new diffusion rates for the surface layer along with the unchanged bulk diffusion rates are plotted in Fig. 5.8. The retention assuming the surface recombination rate from the 100 eV exposures on pure Mo, is simulated and plotted in Fig. 5.9. The reduced surface diffusion can re-create the strong surface peaks from the experimental data, the small amounts of trapped D found past the first $\sim 1 \mu\text{m}$ are overestimated by a factor of $\sim 2-3$ with the simulation for the 500 K and 600 K cases. These problems may be due to some missing physics in the simulation for the situation of a Mo sample ingrained with B. The

Figure 5.8 Diffusion rates for the bulk and surface layer of a Alcator C-Mod tile that yield the best fits to experimental data.

Figure 5.9 Comparison between the experimental data and numerical reproduction for 30 eV/D+ plasma exposures on an Alcator C-Mod tile.

natural hydrogenic solubility of the surface layer may be greatly increased by the large amount of boron present. Also, since it is not known if the boron concentration is a global or a local effect (i.e. concentrated in the grain boundaries or in small clusters), it is difficult to say how the strongly trapped D that was already present will affect diffusion rates out of the surface.

Since the W lamellae was only exposed at a single temperature we have limited knowledge of the temperature dependence of the diffusion rates. We know from the thermal desorption data that the diffusion rate increases only slightly for the elevated temperatures and this would imply the activation energies similar to the boron-rich surface layer in the Alcator C-Mod tile, although likely with a higher coefficient. Still, these diffusion rates are orders of magnitude smaller than rates published in the literature [38, 32]. Since we also have no experimental data for surface recombination rates or the ratio between beam-produced and plasma-produced traps in tungsten, this makes it unfeasible to create any supported model for D retention in W lamellae.

5.3 Fitting Thermal Desorption Data

The thermal desorption data is important in characterizing the thermal-detrapping rate. Now that the diffusion and surface re-combination have been set in the model and the thermal detrapping coefficient has been approximated through physical arguments, the thermal desorption data can be fit to yield a trap energy. The model was started with a total D concentration similar to what was found in the experimental data after the plasma exposure. The final layer boundary condition was also changed from a zero-density boundary condition to a zero-gradient boundary condition. By setting the gradient for the final layer to be zero, particle conservation is enforced and this ensured the only D atoms lost are through thermal desorption. The simulation is run for 250 s (or 300 s in the case of the 100 eV exposure) at a fixed temperature. The total retention after 250 s was then compared to the initial retention and a desorbed fraction was determined. This was performed for all three ion energies. The results are found to rely strongly on trap energy and when compared to experimental data, a trap energy of 1.55 eV has the best fit (see Fig. 5.10). The thermal desorptions at 500 K appears to be underestimated by the model. This may be due to the distribution of D at 500 K, which was more peaked at the surface as opposed to the assumption of a flat D concentration

Figure 5.10 A comparison of thermal desorption rates (presented as the fraction of D inventory desorbed in a single spectrum acquisition time) between experimental data and model simulations.

At temperatures <500 K, thermal desorption is a non-factor in determining retention characteristics.

depth profile in the simulation. The higher surface concentration will mean the D does not have as far to diffuse to reach the surface and that surface recombination will be stronger since it depends on the square of the solute D at the surface. This may allow for small but measurable amounts of thermal desorption to take place at 500 K where the model will not re-produce it using the assumption of a flat initial D depth profile

5.4 Fitting Dynamic Results

The experimental results from the dynamically changing temperature exposures showed that the Mo specimen transitioned across several retention regimes in the single exposure time. A reproduction of this data would be a strong indication that the dynamics and physics of the model are accurate. The model assumes a linear increase in temperature from 300 K to 600 K over the total exposure time. All other factors are left unchanged. Unfortunately, the simulation can

Figure 5.11 Comparison between experimental and simulated data for a 30 eV plasma exposure with linearly increasing temperature from 300 K to 600 K. The labeled times correspond to the x-axis in Fig. 4.23.

only reproduce the results early on in the exposure when the temperature is still low. Once the temperature is ≥ 500 K, the total retention in the first 5 μm is overestimated by the model. This is true for all plasma ion energies (see Figs. 5.11-5.13). However, the shapes of the depth profiles are re-created for all times of the exposure, indicating that the diffusion rates are accurate. This may be an indication that the trapping and detrapping mechanisms are the problem and that one of the activation energies in the model associated with these processes is inaccurate.

In the experimental data, the decrease in retention as the temperature ramped up was explained by the saturation level for the Mo plate decreasing with increasing temperature. This is also occurring in the simulation and is most easily seen in simulation results for D retention as a function of time (i.e. dynamic retention) for temperatures from 300-700 K (see Figs. 5.14-5.16). The simulation indicates the saturation levels as a function of temperature are not fit properly. This is most easily seen by the 500 K dynamic retention. In the simulation the 500 K dynamic retention is just barely starting to turn-over and approach a saturation level, whereas in the experimental data, the turn-over in the data is much clearer indicating it is closer to its saturation level (see Fig. 4.20b). The effects are also seen in the 600 K simulated data where the simulation is very close to saturation by the end of the exposure, but in the experimental data, saturation is reached approximately

(a) 250 - 1000 s

(b) 1000 - 1750 s

Figure 5.12 Comparison between experimental and simulated data for a 100 eV plasma exposure with linearly increasing temperature from 300 K to 600 K. The labeled times correspond to the x-axis in Fig. 4.23.

(a) 250 - 1000 s

(b) 1000 - 1750 s

Figure 5.13 Comparison between experimental and simulated data for a 350 eV plasma exposure with linearly increasing temperature from 300 K to 600 K. The labeled times correspond to the x-axis in Fig. 4.23.

Figure 5.14 Simulated data for D retention as a function of time for all exposure temperatures for a 30 eV plasma.

Figure 5.15 Simulated data for D retention as a function of time for all exposure temperatures for a 100 eV plasma.

Figure 5.16 Simulated data for D retention as a function of time for all exposure temperatures for a 350 eV plasma.

half way through the plasma exposure (See Fig. 4.21a) This indicates an incorrect balance between trapping and de-trapping. The thermal detrapping rate and surface recombination have been fit to experimental data so it is assumed these values are not the issue. The trapping rate is dependent on temperature (through the square root of the diffusion rate) and increases with increasing temperature. Since the depth profiles and the early stages of the dynamic temperature are well fit by this trapping rate, it is thought that the temperature dependent aspect of the trapping rate is the problem rather than the coefficient. However the general trends are still well recreated by the model.

5.5 Simulated Alcator C-Mod and ITER-like Discharges

Using a model allows for the extrapolation to larger and more powerful experiments where the conditions can not be re-created in the laboratory. To test if the unexpectedly high hydrogenic retention rates seen in Alcator C-Mod are due to effects seen in the work on DIONISOS, an Alcator C-Mod plasma discharge will be simulated. The same material characteristics that were used for the Alcator C-Mod tile simulations for DIONISOS are used for the simulated plasma discharge.

Figure 5.17 Deuterium concentration depth profile after a 3 s simulated Alcator C-Mod plasma discharge.

However, since it is unlikely that the boron-rich surface layer will be present in regions of net erosion in Alcator C-Mod, a simulation will also be run with the characteristics used for the pure Mo plate.

While the model can simulate plasma-induced heating, because the heat fluxes are so high and the region of interest so shallow ($5\text{ }\mu\text{m}$) the model quickly becomes unstable when trying to calculate the temperature. For the simulation the temperature of the first $5\text{ }\mu\text{m}$ of the surface were assumed to increase linearly from 300 K to 700 K over the course of a 3 second discharge. The incident plasma flux density was assumed to be $1 \times 10^{23}\text{ D/m}^2\text{s}$ with 50% surface reflection. There are negligible $\sim\text{MeV}$ particles in Alcator C-Mod so the traps produced through surface irradiation are assumed to be zero, but the plasma-produced traps are assumed to scale linearly with plasma flux density based on a pressure-driven trap production method.

The resulting D concentration depth profiles from the simulation of both the Alcator C-Mod tile and the pure Mo plate are shown in Fig. 5.17. The D in the Alcator C-Mod tile is concentrated in the near surface due to the diffusion inhibition in the surface layer. The D in the Mo plate has

diffused to a depth of $\sim 4.5 \mu\text{m}$ and is more distributed over the first few microns of the surface. Since the deuterium did not diffuse to the final layer in either case, the zero-density boundary condition did not come into play. This means that particle conservation is applicable and the total D retention for both cases is the same despite the different depth profiles. The total retention can be presented as an areal density if the total volumetric concentration of D (i.e. the integral under the curves in Fig. 5.17) is multiplied by the depth over which it is measured. In this case the D was measured over $5 \mu\text{m}$. The total D retention as an areal density is simulated for several discharges of varying incident plasma flux is plotted as a function of time in Fig. 5.18. Since the simulated depth is beyond the solute D diffusion range for either the Alcator C-Mod tile or the pure Mo plate in a 3 s plasma discharge, the total retention is the same for both the Alcator C-Mod tile and the pure Mo plate. The results show a linear dependence for the retention as a function of time despite reaching material temperatures as high as 700 K. This is not unexpected since the pressure-based trap production mechanism has a linear dependence on the plasma flux and the time scale for the discharge (3 s) is too short for significant trap annealing or thermal desorption to occur. The final D retention of the discharges in Fig. 5.18 are then plotted as a function of incident fluence (see Fig. 5.19). The result is a linear retention rate of 0.35%, which re-produces the results from the Alcator C-Mod retention study (see Fig. 1.3) although the zero-offset is a factor of two different. This shows the Alcator C-Mod results to be reproducible if an appropriate trap production rate is selected. Since the trap production that reproduces the Alcator C-Mod results is linearly dependent on plasma flux, this is further evidence of a pressure-driven trap production mechanism due to plasma ion implantation.

The other important Alcator C-Mod result is the lack of saturation despite repeated plasma discharges. It is thought the same effects that were seen in the dynamic temperature experiments in DIONISOS are also occurring in Alcator C-Mod. Namely, the temperature ramp will drive trapped D deep into the bulk, and the rapid cooling once the plasma, also the heat source, is removed, the trapped D becomes immobile and is locked at its current depth. Then, it is available to move even deeper into the bulk on subsequent heating cycles. This is re-created in the model. Two consecutive Alcator C-Mod plasma discharges with C-Mod tile diffusion rates were simulated with a 3 s cool

Figure 5.18 Hydrogenic retention as a function of time for a 3 s plasma discharge in Alcator C-Mod for various plasma flux densities.

Figure 5.19 The retained D in a simulated Alcator C-Mod plasma discharge as a function of incident D ion fluence.

down period after each plasma discharge. During the cool down period, the temperature was linearly ramped from 700 K back down to 300 K. The results from the simulation show that after the first plasma the D diffuses to a depth of $\sim 2 \mu\text{m}$ and after the second plasma discharge the D is now trapped down to a depth of $\sim 4 \mu\text{m}$ (see Fig. 5.20). Another interesting effect is seen during the cool down period. As the tile cools down, the D trapped deep in the material actually increases slightly. This is thought to be due to the presence of available trap sites when the plasma discharge finishes at a temperature of 700 K. As the temperature decreases, the thermal de-trapping rate decreases exponentially allowing all available traps to become filled again. The solute D that is deep in the material becomes relatively immobile when cooled quickly but it is still able to fill nearby traps. Essentially, after a rapid cooling, it is more likely for solute D that is deep in the bulk to fill available trap sites than to diffuse back to the surface and recombine. This effect could also explain the slight rise of D retention in the first $5 \mu\text{m}$ seen in the experimental results from DIONISOS for the dynamic temperature experiments (see sec. 4.5). The retention from the consecutive plasma discharges also shows no saturation in the overall retention of the Alcator C-Mod tile (see Fig. 5.18). Again, this recreates the retention results that were seen with "bare Mo" Alcator C-Mod walls.

The surface conditions created in DIONISOS more accurately re-create conditions in ITER in the respect that there is simultaneous plasma exposure and irradiation of the surface by MeV-energy particles. Since the model has shown itself to be capable of accurately reproducing results for surfaces undergoing simultaneous plasma exposure and irradiation, it may also be useful to have it re-create an ITER-like plasma discharge. The simulated plasma discharge had a duration of 300 s. The temperature was ramped from 300-600 K in the first 75 seconds of the discharge when it is assumed plasma current ramp-up is taking place. For the remainder of the discharge the temperature is held at 600 K since the PFC tiles will be actively cooled. This is not truly accurate for an ITER discharge. Since the plasma is the source of particles *and* heat for the PFC, the heat load is applied to the surface of the PFC tile. The heat is removed through the back of the tile into the water-cooled heat sink. This results in a temperature gradient from the front of the tile to the back of the tile. The temperature gradient will come to an equilibrium and the magnitude of the

Figure 5.20 The D concentration depth profiles after consecutive plasma discharges in Alcator C-Mod, and after the cool down period between the two discharges.

Figure 5.21 The total D retention of an Alcator C-Mod tile after consecutive plasma discharges with a 3 s cool down period between discharges.

gradient is determined by the thermal conductivity of the PFC. Investigations into the effects of a temperature gradient as a function of depth on retention properties is beyond the scope of this study. A plasma flux density of 1×10^{23} D/m²s was assumed and the D retention was simulated over the first 200 μ m of the surface. The PFC material is assumed to be pure Mo with no surface oxides or impurities since it is thought that any thin layers on an ITER PFC will rapidly be removed by the plasma. This means that the bulk Mo diffusion rates are used for all layers in the simulation. In ITER, during D-T burn operations the walls will be irradiated with 14 MeV neutrons. Neutron irradiation will distribute damage evenly throughout the entire PFC. A dpa rate of 2×10^{-7} dpa/s was used based on the assumptions that ITER experiences ~ 1 dpa/year, and operates 6 hours a day, 5 days a week, and 45 weeks a year. This is approximately consistent with the 0.5 MW/m² neutron wall loading expected for a full D-T ITER discharge. This dpa rate is set to be distributed in a flat profile over the entire 200 μ m depth in the simulation, given the stopping range of MeV neutrons is on the order of meters in the PFC wall, but is still subject to the 1/4-power dependence and 0.00015 conversion coefficient found from DIONISOS experiments for the conversion from dpa to trap sites.

The D concentration depth profile at the end of the simulation is shown in Fig. 5.22. The D is trapped down to a depth of 110 μ m in the surface, at which point the trapped D rapidly goes to zero. The 110 μ m is the maximum depth that solute D can diffuse to in the 300 s discharge time. Since the neutron irradiation is uniform, the trap sites are filled down to the diffusion limit of the D. This is shown by the flat profile between 40 μ m and 100 μ m. Near the surface the retention is much higher due to the plasma-produced trap sites, and these trap sites are seen to diffuse to a depth of ~ 40 μ m in the 300 s discharge. Plotting the areal retention as a function of time shows this also follows a linear retention rate (see Fig. 5.23). This is unexpected since the DIONISOS data indicates saturation should be approached for 600 K temperatures. However, it is noted in Fig. 5.22 that the D trapped in the neutron traps is only at a concentration of $\sim 7 \times 10^{25}$ D/m³ and the saturation level shown in DIONISOS for 600 K exposures was $\sim 1.5 \times 10^{26}$ D/m³ (see Fig. 4.21a). Therefore, saturation levels have not been reached in much of the bulk of the tile, making a linear increase of retention with fluence a reasonable result in this case. The relative rate

Figure 5.22 Deuterium concentration depth profile after a 300 s simulated ITER plasma discharge.

Figure 5.23 Hydrogenic retention as a function of time for a 300 s simulated ITER-like discharge.

of D retention is $\sim 0.9\%$ retained D per incident D ion, a result which is very similar to the Alcator C-Mod experiments, but higher due to the effect of neutron-induced damage in the bulk. The simulation indicates concentrations at the surface that are reaching ~ 0.05 D/Mo. At these sorts of trap densities the material properties may begin to change or blister, which is not accounted for in the simulation. Regardless, the final retention indicates that if the plasma was 50% tritium, there would be $\sim 1.35 \times 10^{23}$ T/m², or ~ 0.67 g/m² of T, retained in the walls for each plasma discharge in ITER. If this type of retention rate is occurring in even 10% (100 m²) of the ITER wall, the tritium inventory limit will be reached in five 300 s discharges. This effect is being set by the distributed trap productions from the neutrons being simultaneous with high plasma flux density to the surface and elevated temperatures for long durations. These are conditions which are not recreated in any present tokamak experiment and so may not be seen until ITER begins operation.

Chapter 6

Discussion

6.1 Ion Beam Trap Production

One of the most important aspects of this study is the quantification of the relationship between irradiation damage and trap production. Without accurate experimental data and theory, the hydrogenic retention characteristics of future tokamak devices, in which energetic particles will be irradiating the wall, can not be accurately predicted.

In this study the target was irradiated with a ^3He ion beam of a known energy. This allowed the irradiation damage in the target to be accurately calculated. With the simultaneous ^3He irradiation and D plasma exposure the effects of the irradiation on effective deuterium trap production can be measured in real-time in the near-surface region by NRA.

The results (see sec. 4.1.2) show that the trap production can be related to irradiation damage through a linear relationship, a square root relationship, or a 1/4-power relationship to acceptable accuracy. Modeling the results showed that the best reproductions to the experimental data were found with the 1/4-power relationship. The work by Oliver et al. [68, 69] showed that there was no change in the trap density in W from 0.31 dpa to 7.9 dpa. This implies a rapid approach to saturation of trap density resulting from irradiation damage. This strongly supports the 1/4-power relationship that would result in a fast approach to saturation. However, it was clear in the present study that trap density saturation levels were not reached despite damage levels of >1 dpa. However, this study was performed on Mo, which may indicate a difference in irradiation resistance between the two materials. The work by Takagi et al [49] was performed on Mo. It showed a relationship between trapped D and dpa level that was closer to a square root dependence.

They measured to a dpa level of 13 dpa and the Mo target had still not reached saturation. This damage was highly concentrated in the first $\sim 1.5 \mu\text{m}$ of the surface with a highly peaked spatial distribution.

When Takagi et al. fit a linear relationship between irradiation damage and trap production they found a conversion factor of 0.007 for displacements to be converted to trap sites. In the present study the conversion factor was found through modeling of experimental results to be 0.00015. The difference is likely due to the different dependencies (i.e. linear for Takagi, 1/4-power for the present study) and possibly from the different irradiation energies (i.e. 0.8 MeV for Takagi, 3.5 MeV for the present study). Both the present data and the results from Takagi were taken at a Mo temperature of 500 K, however, it is probable that there will also be a temperature dependence on the conversion factor as was indicated in sec. 4.1.1. It will be a crucial contribution to the database of tokamak operations if a conversion factor as a function of material temperature, starting material properties, and ion/neutron energy, for the production of trap sites from high-energy ion/neutron irradiation can be measured. This would be high priority work for future work on the DIONISOS experiment.

6.2 Deuterium Retention as a function of Surface Temperature and Plasma Ion Energy

The temperature dependence of hydrogenic retention is the key to quantifying many of the controlling processes. Diffusion, surface recombination, and thermal de-trapping and desorption are all exponentially dependent on temperature. These values and their balance with one another dictate where the D is trapped, what conditions are required to remove it from the target, and the retention saturation rates in Mo.

The ability to produce depth-resolved density profiles over the first $5 \mu\text{m}$ of the surface in real-time allows for the mobility of the D (and consequently the trap sites) in the surface to be measured as a function of temperature. By fitting these depth profiles with a 1-D, flux conservation slab model, a diffusion equation was found for D in Mo (see eq. 5.3). This H/D diffusion rate in Mo is in line with rates seen in literature (see Fig. 6.1). The diffusion rates that most closely

Figure 6.1 The diffusion rate of D in bulk Mo as determined by fitting of experimental results from DIONISOS is compared to a number of published diffusion rates for H/D in Mo.

agree with our values are those found by Caskey via D permeation through an electron-beam melted Mo foil [34], Tanabe via ion-driven permeation of D through Mo [35], and Stickney via D permeation through Mo foils. The general agreement with literature gives confidence to our experimentally fitted diffusion rates and to the technique of determining diffusion rates through temperature-dependent depth profiles.

Now that the diffusion rates for the surface and bulk regions are known, the model by Shu et al. can be used to determine the retention regimes for the experiments (see sec. 1.2). The recombination rates are taken from the experimental data and the implantation range is assumed to be 10 nm. Since the incident flux density and the thickness of the samples are well known, we can solve for U, V , and X from equations 1.15-1.17 for different Mo temperatures (see Fig. 6.2). Recall from sec. 1.2 that the RD-regime (i.e. Recombination limited on the front surface and diffusion limited on the back surface) applies for values of $U < 1$ and $V < 1$. This is the case for the majority of the temperatures in this study. However, at temperatures $\lesssim 400$ K, $U > 1$, meaning the RD-regime no longer applies. At temperatures $\lesssim 400$ K, $U > 1$ and $UVX < 1$ meaning the DD-regime

Figure 6.2 The U, V, and X factors defined by Shu et al. (see sec. 1.2) to determine the limiting process for the front and back surfaces of the specimen. These factors are for the 30 eV/D+ plasma exposures and it is found that the values are very similar for the 100 eV/D+ and 350 eV/D+ plasma exposures.

now applies. These findings are similar for all ion energies with the temperature for the transition from the RD-regime to the DD regime increasing by ~ 20 K as the ion energy is increased from 30 eV to 350 eV. These results support the findings from the experimental data where it was found that the retention in the first $5 \mu\text{m}$ of the surface was diffusion-limited at 300 K, but at 400 K, diffusion was no longer the limiting process.

The depth profiles are re-created accurately by the model although there appears to be over-estimation by the model for the higher Mo temperature cases. It is suspected that this over-estimation of the high temperature retention may be due to improper temperature dependences and/or activation energies for key processes, one of which being the rate at which solute deuterium occupies trap sites. The model does not account for any history effects in the samples either. In sec. 4.2 there was evidence for a history effect from comparing the "re-do" results for the 30 eV case to the original 30 eV results. Any history effect would mean the DIONISOS retention results

are actually higher than one would expect if a new target was used for each exposure making the model fits even worse. However, there are other factors at these high temperatures that must be considered. The model is confined to one dimension, but diffusion is a 3-D process. Since the plasma flux density is peaked in the center of the column, there is a D density gradient present that can drive lateral (i.e. parallel to the surface) diffusion. Lateral diffusion is not accounted for in the 1-D model and at low and intermediate temperatures it is unlikely to play a role since the diffusion length-scale, $\sqrt{D \cdot t}$, for 1500 s will still be $<100 \mu\text{m}$, but at high temperatures (i.e. 600-700 K), the diffusion length scale can reach up to $\sim 0.5 \text{ mm}$, meaning significant amounts of D could diffuse out of a 2 mm radius beam spot centered in the plasma column. It is possible that this effect is dominating any history effects making the over-estimation by the model a reasonable expectation. In a more detailed model both lateral diffusion and history effects could be accounted for, provided the necessary experimental data to quantify these effects is available.

The total retention rates that are seen in the DIONISOS experiment are higher than those typically seen in laboratory experiments (as opposed to fusion/tokamak experiments) at these ion fluences [52, 46]. The key difference in the DIONISOS experiment is the presence of high-energy particles, namely the 3.5 MeV ^3He ion beam. An external beam with variable energy and fluence is highly useful tool in two ways. First it is a scientific tool in that it gives the experiment the ability to accurately calculate and manipulate the displacement profile. Correlating resulting effects on retention allows for nearly direct extraction of important parameters such as traps/displacements and trap mobility. Secondly, the beam can be used as an experiment simulation of the damage foreseen in fusion reactors. It has been shown that this high-energy ion irradiation creates mobile trap sites deep in the surface that can diffuse well beyond the plasma ion implantation range. These traps are then filled by D ions implanted by the plasma and proceed to diffuse into the bulk. This re-creates conditions in a fusion reactor where wall materials will be subjected to simultaneous plasma and high-energy ion/neutron irradiation.

The results from DIONISOS also show that the plasma alone can create mobile traps at densities far in excess of the expected natural trap density on Mo. This plasma-driven trap production was found to have no dependence on plasma ion energy implying that traps are not being produced

through physical collisions between the plasma ions and the Mo lattice atoms. This led to the hypothesis of a pressure-driven trap production mechanism in sec. 4.2.3. In the model, it was assumed that a pressure-driven trap production mechanism would scale linearly with plasma flux density. The reasoning being that if the ion energy is constant, then the implantation zone would remain constant in size, but if the plasma flux density was increased, then there would be a greater number of D atoms in the same confined space resulting in higher pressures. Therefore at constant surface temperature, and therefore constant thermalized temperature for the implanted D, the pressure scales linearly with density and therefore flux density. Temperature will also affect pressure and this is not accounted for in the model, mainly because temperature also has an exponential effect on hydrogenic diffusion. In the case of D-ion implantation in Mo, diffusion is the "relief valve" for the implantation zone. As temperature increases, the D will leave the implantation zone at a greater rate causing the peak pressure to go down. Since the diffusion rate has an exponential dependence on temperature and pressure has a linear dependence, it is expected that the diffusion effect will dominate at some higher temperature. This is hinted at by the data in sec. 4.1.1, where it appears that the plasma is responsible for 10-20% of the trap production at 500 K and 30-40% of the trap production at 400 K. This effect is further complicated by the temperature dependence on the trap mobility. In the model this temperature dependence is assumed to balance out leaving the plasma-induced trap production rate only dependent on plasma flux density. A more detailed examination of this effect would be appropriate for future studies.

The modeling of the 100 eV plasma exposures is a good test case for this theory. Since the 100 eV plasma exposures were performed at 50% higher plasma flux densities and $\sim 60\%$ lower irradiation fluence, the model can re-create the new balance between beam-produced traps and plasma-produced traps. With the excellent agreement between the model and the experimental data (see Fig. 5.7), a strong case can be made for the concept of pressure-driven trap production. *This is one of the most critical results from the DIONISOS experiments.* If a trap production mechanism scales linearly with plasma flux density, then this will have major impact on retention levels in tokamak experiments where flux densities are typically orders of magnitude higher than found in laboratory plasmas or ion beams.

The Alcator C-Mod tile is more difficult to model due to the added complication of having 12% boron in the first $0.5\ \mu\text{m}$ of the surface. The presence of the boron can not only reduce hydrogenic diffusion through that region of the surface but could also increase the natural solubility of hydrogen in that layer. The model can include a reduced diffusion rate in the surface layer, but it works under the assumption that solubility is negligible in terms of hydrogenic retention. This assumption is valid for Mo, but boron has a much higher hydrogenic solubility (i.e. $\sim 0.1\text{--}0.2\ \text{D/B}$) and this could be playing a role in the retention profiles. The presence of $\sim 0.7\%$ D/Mo in the boron-rich layer that can not be thermally desorbed at the temperatures available to the DIONISOS experiment, is evidence of a high-energy trap site that is not created by either the ion beam irradiation nor the DIONISOS plasma. It is clear that the high-energy traps are associated with the boron and that these are playing an important role in the retention behavior of the Alcator C-Mod tile. For the modeling, the deuterium in the high-energy traps is ignored since it is assumed to never be released. It is unclear if the density gradient from this D near the surface is contributing to diffusion or not. The fits between the DIONISOS results and the model are for the *net* hydrogenic retention of the tile (i.e. after subtracting the constant D content in the B containing surface layer). The fits for the Alcator C-Mod tile re-create the trends seen in the experimental data, namely the strongly peaked D concentrations at the surface and small amounts of D traveling deeper into the bulk to beam-produced traps, but the magnitudes of the deep D are over-estimated by the model.

One aspect of the effects of the boron that was mentioned in sec. 4.2.3 and sec. 5.2 is the specific location of the boron. The model can not compensate for local effects, it assumes a uniform surface. If the boron is spread uniformly throughout the first $0.5\ \mu\text{m}$ of the surface this would have a far different effect than if it was collected in small pockets or grain boundaries. The uniform distribution of boron would be more likely to inhibit hydrogenic diffusion into the surface. If it is a local effect, the majority of the D would diffuse around it and it would have little impact on the overall diffusion rate. One exception to this is if the boron is locally collected in grain boundaries. If the grain boundaries are the primary means of diffusion into the bulk then the overall diffusion could be inhibited if the grain boundaries are full of boron. The impact of solubility will also depend on the location of the boron. If the boron is a local effect, there will be pockets of high

hydrogenic solubility that may influence the overall solubility of the surface layer. If the boron is spread uniformly throughout the Mo, it is unlikely it will increase the natural solubility of Mo enough to be significant. DIONISOS does not have the facilities to determine the exact location of the boron, but it is recommended that this factor be given high priority in future studies of the impact of ingrained boron on hydrogenic retention. Understanding the role of low-Z coatings (i.e. boron) on high-Z materials (i.e. Mo) is also a high priority for future studies, in particular since the presently envisioned use of W in ITER will be coincident with Be and C PFC surfaces, and they will likely accumulate on some W surfaces, with a similar impact to B on Mo in Alcator C-Mod.

The W lamellae specimen did not have enough available data to be fit properly by the model. The fact remains that the W showed the lowest retention rate at 400 K of any of the specimens examined. This was largely due to the diffusion, which appeared to limit the deuterium to the first $\sim 2 \mu\text{m}$ of the surface. It is not clear why the diffusion appears to be so low, and despite heating the W up to 720 K it still did not appear to diffuse past $3 \mu\text{m}$. It is suspected that either the surface polishing of the lamellae structure or the W is limiting diffusion. Clearly more work needs to be done on W as this material will be used in the ITER divertor design. If the W used in ITER has the same retention characteristics as the W lamellae investigated in DIONISOS, then this will be beneficial for the operation of ITER. Retention will not only remain low but close to the surface where it is more easily removed. However, given the apparent contradiction in diffusion rates between the DIONISOS results and those published in the literature, it is important that more controlled experiments be performed on W in DIONISOS before any conclusions are made.

6.3 Thermal Desorption

The thermal desorption data yields the trap energy of D traps in the Mo. This value is important for determining the rate of thermal desorption but, more importantly, determining the thermal de-trapping rate as a function of temperature. The thermal de-trapping rate is one of the key characteristics that dictates saturation levels at various temperatures. The thermal desorption was most accurately recorded and modeled for the Mo temperatures of 500 K to 700 K, where its effects are the strongest. At temperatures below 500 K, thermal desorption did not play a significant role.

At elevated temperatures, the experimental data is fit well assuming a trap energy of 1.55 eV. This value is in line with the literature, which quotes values ranging from 1.0-1.4 eV [46, 47, 48, 49, 50]. If the trap energy were closer to 1.4 eV, this would result in lower saturation levels in the model than if the trap energy was assumed to be 1.55 eV. A slight over-estimation of the trap energy may be contributing to the over-estimation of retention levels at high temperatures in the experimental data. In future, the model would be better served if it was fit to data from a more controlled thermal desorption process. Another possibility would be the introduction of more than a single trap energy, but this requires more data in order to sufficiently constrain the fits based on the simulations.

6.4 Dynamic Retention

The hydrogenic retention properties of a material are a balance and interaction of a number of rates: diffusion rate, surface recombination rate, thermal de-trapping rate, and trap production rate. This makes time a key aspect of the equation. DIONISOS is positioned uniquely to measure the hydrogenic retention of a surface in real-time and investigate the dynamic effects of hydrogenic retention directly. The numerical model used in this thesis is based on a time-step loop allowing it to also reproduce dynamic effects given the time-scale is not too short.

The measurement of retention as a function of time can reveal information about the retention rate-limiting process and the saturation level. The saturation level is a balance reached between the rate at which soluble deuterium occupies available trap sites and the rate at which trapped deuterium is thermally de-trapped. This balance will evolve as the number of traps and the amount of soluble deuterium evolve, but at some point an equilibrium will be reached. The important question is where this equilibrium will end up. In sec. 2.3, it was mentioned that in the literature, for all experiments measuring hydrogenic retention as a function of incident fluence on Mo, a saturation level was never reached. It was thought originally that this may indicate the formation of unsaturable traps such as bubbles and blisters, but in sec. 4.6 it was concluded that blistering is not affecting the retention properties of the Mo.

Figure 6.3 Comparison of high temperature results for 350 eV/D+ plasma exposure simulations for a model assuming a zero-density boundary condition and a zero-gradient boundary condition.

In the experimental results from DIONISOS, an equilibrium retention was reached in the first 5 μm of the surface at temperatures of 600 K and 700 K. An important point to remember is that this equilibrium/saturation is only measured in the first 5 μm of the surface and does not necessarily mean the global retention levels have also reached saturation. The model demonstrates that much of the trapped D is not lost back to the surface but "lost" into the bulk of the Mo beyond the range of detection for 3.5 MeV ^3He NRA. This is shown by changing the model's boundary condition on the last layer. A zero-gradient boundary condition enforces particle conservation by not allowing any particles to move past the final layer and the only loss of particles coming from surface recombination at the surface. A zero-density boundary condition causes the last layer of the model to act as an infinite sink and particles can be lost either to the infinite sink or through surface recombination. The retention levels at high temperatures for the zero-gradient boundary condition are far greater than the retention levels for the zero-density boundary condition (see Fig. 6.3). This leads to the conclusion that at high temperatures, based both on the flat experimental D profiles and the simulation results, that a large portion of the retention is occurring deeper than 5

μm into the surface. This result is not surprising given the high mobility of D in refractory metals, as temperature increases, the deuterium's range in the metals becomes very large. This highlights an important feature for using refractory metals in a plasma/fusion environment. Overall, the trends of the dynamic retention data are re-created by the model. This is an indication that the balance and relative magnitude of the key rates for retention properties are correctly predicted.

Another effect that can be captured by the real-time measurements by DIONISOS is the surface recombination. If surface recombination is the rate-limiting process for deuterium to leave the surface during a plasma exposure then there will be a sudden drop of D concentration in the surface layer when the plasma is turned off. This can be measured, although rather coarsely over the first 250 nm of the surface, directly by DIONISOS and surface recombination rates can be derived from that data. The rates defined by the experiment were entered directly into the model. The surface recombination rate was the only data that had any dependence on plasma ion energy. It was found that the surface recombination rate increased with increasing ion energy. It is thought that this effect is caused by the sputtering of the surface oxide/impurity layer. For the three ion energies the sputtering yield increases significantly over the range of energies. At the highest energy, 350 eV/D+, over a 1500 s plasma exposure, approximately 45-135 nm of Mo will be sputtered from the surface. The results from the XPS study of the surface show that there is a large impurity content on the surface and corresponding ion beam analysis estimates this layer to be ~ 10 nm thick (see sec. 4.6). So, for the highest ion energies, one would expect a clean Mo surface during and immediately after the plasma discharge. A clean surface will have the highest surface recombination rate and that is seen in the experimental data. The model also confirms this in an indirect way. In the model, the presence of the surface oxide/impurity layer is represented by a layer of reduced diffusion, the same as it was for the Alcator C-Mod tile although different surface diffusion rates were used. However, for the 350 eV experimental data, the fit was found to be improved if this layer of reduced diffusion was removed and the bulk diffusion rates were used for the entire model. This suggests a sputtered clean surface for the 350 eV/D+ plasma exposures. It is interesting to note that while there is no dependence of the retention levels on ion energy, the ion energy can influence both the surface recombination rate and diffusion rate near the surface through sputtering effects. Although

no surface recombination rates for Mo were found in the literature, a surface recombination rate for W was found [43]. The surface recombination rates from the experimental data are ~ 10 orders of magnitude lower than those cited for W. Despite such a large difference in values, it is not entirely unexpected since surface recombination is an extremely difficult process to measure and it is also very sensitive to a number of other factors that were not closely monitored in this experiment. Large scatters in recombination results are seen for other materials, such as iron, where predicted recombination rates can vary as much as six orders of magnitude for the same material [15, 16]. So, it seems quite possible that the surface recombination could vary by 10 orders of magnitude for two different, but similar, materials such as W and Mo. The important aspect for tokamak and future applications is that surface recombination is limiting the rate at which D can escape the surface. This results in a build-up of un-trapped D at the surface that could suddenly be released into the plasma were the surface recombination characteristics to change (such as sputtering has done in the 350 eV/D⁺ plasma exposures in DIONISOS) or the temperature to spike suddenly. DIONISOS is able to measure this dynamic retention in real-time under plasma conditions. This could be a key aspect of understanding plasma fuelling and fuelling instabilities in a long-pulse or steady-state tokamak.

6.5 Dynamic Surface Temperature

Hydrogenic retention is an inherently dynamic process, but in a tokamak environment the surface conditions that dictate the hydrogenic retention properties will also be changing dynamically. In a tokamak with inertially cooled tiles, the temperature will ramp up with plasma exposure. Since many of the rates that determine retention properties are exponentially-dependent on temperature, the retention characteristics can change drastically over a single plasma exposure. With the active temperature control on the DIONISOS sample holder, this situation can be re-created experimentally.

The experimental results from DIONISOS demonstrate how the changing temperature can change the retention characteristics in a single plasma exposure. As the temperature ramps up from 300-600 K, the retention progresses from diffusion-limited, to linear increases of retention

with time (and fluence), to equilibrium in the first 5 μm of the surface. The model does not reproduce the experimental results exactly, but many of the trends are re-created, including changing depth profiles as the temperature increases. The one aspect that the model misses is the reduction in retention in the first 5 μm once the temperature increases above 500 K. In the model, the retention only begins to slightly decrease when the temperature reaches ~ 600 K. This mismatch indicates one of the key processes in determining the saturation level is incorrect in the model. In sec. 6.3, it is suggested that the trap energy may be overestimated in the model based on trap energies found in the literature. A lower trap energy would lead to higher thermal de-trapping rates and result in saturation being reached at a lower temperature. A similar effect would be seen if there were two or more trap types with different trap energies. Another possibility is the rate at which soluble D occupies available trap sites (i.e. the trapping rate). This rate was not based on any experimental data or values from the literature, but on simple physical arguments. It is possible the trapping rate has been over-simplified and over-estimated or with the incorrect dependence on temperature.

An important observation from our modeling efforts is that it shows that if all other values are known with confidence, the trapping rate can be left as the only free variable. Then a model similar to the one used in this study would be able to fit the trapping rate based on dynamic data taken from the experiment. This is a perfect example of how DIONISOS allows dynamic rates and processes that could never be seen in ex-situ or "post-mortem" experiments, to be investigated and measured in a controlled manner.

6.6 Consequences for Alcator C-Mod, ITER, and Beyond

Despite the high level of control that DIONISOS has over surface and plasma conditions, it can not re-create a tokamak environment. The control over experimental conditions allows for the important processes and behaviors to be measured as a function of experimental parameters. Once these behaviors are quantified, a model can be created to extrapolate these results to tokamak conditions. This was performed in sec. 5.5.

One of the key differences between tokamaks and laboratory plasmas is the large difference in plasma flux density. Since the plasma flux density in a tokamak divertor is an order of magnitude

or more higher than laboratory plasmas, the plasma in a tokamak divertor brings both particles and heat to the surface. Temperature has been shown to strongly affect many aspects of hydrogenic retention, making it important to understand how and where the PFC surface is being heated. This surface heating via plasma can also lead to strong temperature gradients from the surface to the back of the PFC tile if the tile is being actively cooled, as they are in ITER. These are conditions that are extremely difficult to re-create in a laboratory but can be incorporated into a well-established model.

Alcator C-Mod can operate at very high flux densities in the divertor ($\leq 10^{23}$ D/m²s). At these flux densities and a plasma electron temperature of $T_e \sim 10$ eV, this translates to ~ 1 MW/m² of heat flux to the surface. As a rule-of-thumb, 1 MW/m² translates to ~ 100 K/s temperature ramp for inertially cooled tiles. Due to numerical limitation of the model being used in this study, this was simulated as a linear temperature ramp from 300-600 K for the entire depth investigated for a 3 s plasma discharge.

The results from the modeling of a Alcator C-Mod plasma discharge yield important insights to the retention mechanism that could occur in a tokamak divertor with inertially cooled walls such as Alcator C-Mod. The plasma exposure brings both high particle flux, and hence surface trapping, simultaneously with ramping temperature which allows for the migration of the traps to deeper locations. The sudden removal of the heat is coincident with removing the particle source, however the short cool down times prohibit substantial release of the trapped D, resulting in the D being "frozen" into the material. Each subsequent plasma discharge and thermal cycle will allow this trapped D to move deeper into the tile. This "ratcheting" effect could be an explanation of why the "bare Mo" wall of Alcator C-Mod did not saturate (see Figs. 1.2 and 1.3). High temperature baking is not available on C-Mod making it difficult to remove D that has been trapped deep in the wall. Based on our experimental and modeling insights, it is the coincidence of particles and heat found in the Alcator C-Mod divertor and the dynamic response of the material to the D influx, which permits high retention rates. The 0.35% linear retention rate that was seen in Alcator C-Mod fuel retention experiments is re-created through the assumption of a trap production mechanism

that scales linearly with plasma flux density. The experimental support for this assumption has already been outlined.

Another interesting result is that the reduced diffusion in the surface layer makes no difference on the overall retention. If the traces in Fig. 5.17 are integrated, the both have the same retention. This is different than what was seen in DIONISOS, where the Alcator C-Mod tile had significantly less retention than the pure Mo plate (See Fig. 4.11). This can be attributed to the presence of energetic particles irradiating the surface in DIONISOS but not in Alcator C-Mod. In DIONISOS, the majority of trap sites were produced by the ion beam at a depth far greater than the plasma ion implantation depth. This means that the implanted D is required to diffuse, sometimes several μm , into the surface before locating an available trap site. If diffusion is limited then this would cause the rate of trapping to also be limited. In the simulated Alcator C-Mod plasma discharge, the plasma itself was the only source of trap production. All simulated traps were formed in the surface layer where the implanted D had immediate access to them. This means that in DIONISOS there is the possibility of unfilled traps in the bulk of the materials if diffusion is a limiting process, but in Alcator C-Mod, since the traps are assumed to be created at the ion implantation depth, they are immediately filled. This implies that for Alcator C-Mod, diffusion dictates where the trapped D migrates but has no effect on overall retention. This also agrees with Whyte et al. who found that the retention levels for boron-coated walls and "bare Mo" walls in Alcator C-Mod, were approximately equivalent [23]. This implies that the reduced D diffusion in the boron coating has no effect on the overall retention level of the Alcator C-Mod wall. The overall agreement between the model and the results from Alcator C-Mod are very encouraging for the validity of the model and the experimental results from DIONISOS.

Using the model to predict retention properties for future devices, such as ITER, becomes more difficult. Mostly because the surface conditions in ITER are not well-known. With a multi-material PFC wall, there will be significant material mixing in ITER, meaning at any point the surface will likely be composed of a combination of Be, W, and C. Also, the ITER PFC tiles are actively cooled, meaning there will be a temperature gradient from the surface of the tile to the heat sink. Neither of these effects are presently taken into account in the model, but could be implemented in future

versions. The temperature is assumed to ramp linearly to 600 K over 75 s and remain constant at 600 K for the remainder of the discharge over the entire target. Future studies should properly examine the interplay between particle flux, heat ramps and cooling in a self-consistent manner given the importance of temperature in retention characteristics. The surface is also assumed to be a pure material in the simulation. The principal insight of importance for fusion applications is the importance of the trap production caused by neutron-produced displacements. This is a poorly understood area of hydrogenic retention but of critical importance for DT operation of ITER and future devices. If the neutron irradiation produces traps per displacements at the same rate as the ^3He irradiation in DIONISOS, then the neutron irradiation can be easily modeled since it will be evenly distributed throughout the PFC tile.

The experimental results and simulations show that the irradiation has a major impact on the retention levels. This was expected from the work performed on DIONISOS but the impact of the uniform distribution of damage demonstrates the importance of understanding how irradiation affects the retention characteristics of a material. After a 300 s plasma discharge, the diffusion tail from the plasma-driven trap production at the surface can be seen to reach $\sim 40\ \mu\text{m}$ into the surface. The D trapping from the neutron irradiation is apparent down to $\sim 110\ \mu\text{m}$, which is the diffusion limit for D over 300 s of the previously mentioned temperature ramp. The PFC tiles will be actively cooled in ITER, so the temperature will return to room temperature very rapidly after the plasma exposure, resulting in D/T trapped and immobile deep in the PFC tile, very similar to the effect predicted by the model in Alcator C-Mod. It is likely subsequent plasma discharges will push the D deeper into the PFC tile where the neutron irradiation will have made available traps. The model shows that even after 300 s of neutron irradiation, the trap density has already reached 0.1% traps/Mo throughout the entire tile and the plasma has produced a trap density as high as $\sim 5\%$ at the surface. Even if a uniform trap density of just 0.1% traps/Mo is assumed to be the saturation point and ignoring all plasma-produced trap sites, if it is assumed that all these traps will eventually be filled by D and T in an equal ratio in a 1 cm thick PFC tile, this would result in a T retention of $\sim 1.5\ \text{g/m}^2$. This means that only $\sim 230\ \text{m}^2$ of the $1000\ \text{m}^2$ interior of ITER would need to display these retention characteristics to reach the 350 g T inventory limit. Assuming the D diffuses ~ 100

μm deeper for each discharge (based on Fig. 5.22), the entire 1 cm PFC tile will contain trapped D/T in ~ 100 plasma exposures. However, the work on DIONISOS suggests the saturation levels of traps produced through irradiation to be much higher than those achieved in a single ITER-like plasma discharge such that the inventory of D/T in the tiles will continue to increase with subsequent discharges. This is a direct consequence of the nature of exposing materials in a fusion environment. The ingredients for high hydrogenic retention, namely large plasma flux density, neutron-induced damage, and high material temperatures, occur simultaneously during plasma operations.

It is important to understand that the retention mechanism that has been outlined here will eventually reach saturation. Such saturation is clearly seen in the experiments (in the near surface), but also can be understood from the physical mechanisms responsible for the retention. The retention is set by the competition between trap production/mobility, the diffusion of D/T through the material and the thermal desorption/detrapping rate. Steady state PFC temperatures will occur in the near steady-state conditions expected in a reactor, so at some time the trapped D/T will come to an equilibrium level in the material, i.e. the retention appears to saturate and the wall no longer can "pump" fuel. This is a fundamentally different retention process than codeposition of D/T in films that are produced by erosion and deposition at the PFC surface, a major concern for low-Z PFC materials such as carbon. In theory the codeposition process will not saturate, since it is really dictated by the buildup of plasma-deposited films in a D/T rich environment, not permeation of the D/T into the bulk material. It is presently believed that codeposition is the dominant process in setting D/T retention for low-Z PFC tokamaks, which are particularly prone to this process because they tend to have higher net erosion and film growth rates and the high solubility of D/T in low-Z films.

The present strategy is to maximize high-Z PFC coverage in ITER and future reactors in order to minimize the impact of T retention. While this strategy is clearly favorable for limiting codeposition, it is unclear from our results and that of Alcator C-Mod whether or not this is, by itself, a viable strategy for controlling the T inventory in PFC materials. The amount of tritium retained in PFC must be limited for both safety reasons and tritium self-sufficiency.

We note that in many ways the observation that bulk retention of D/T will occur in refractory metals is not a surprise, nor is the fact that nuclear-induced damage could affect retention. What was not evident was that the "quantity" of this effect could be so large as to, for example, produce wall pumping rate in a refractory metal tokamak similar to what is seen in low-Z PFC tokamaks. The key point is that *both* retention mechanisms (co-deposition and plasma-driven permeation to neutron-induced trap sites) need to be quantified for predicting and controlling T inventories and this work provides a key step in developing a better understanding and extrapolation capability for the latter process. A general observation is that the ambient temperature for both low-Z and high-Z PFC applications will need to be increased substantially from the near RT of present experiments. Since this ambient temperature of actively cooled PFC tiles during plasma operation has technological limits, it is fair to state that the accurate quantification of what temperature will be required for T control will likely strongly influence the decision for the use of low-Z versus high-Z PFC in future devices. This appears to be one of the most critical scientific missions for fusion PSI research.

It is clear that the introduction of energetic particles will drastically change the retention properties of a material. This raises the question about how best to approach the operation of ITER. Operation of ITER with the current PFC configuration is very unforgiving to disruptions. The current plan is to perfect stable operation of the plasma during DD operation where the neutron flux irradiating the walls is a factor of ~ 100 less than for DT operation. Since a wall with net retention will behave as a particle pump for your plasma, the retention properties of the wall will strongly impact the operation and stability of the density of the plasma. This would apparently undermine the validity of perfecting plasma operation for DT discharges using operating parameters found for DD discharges. The increased neutron flux from the DT discharges will change the retention properties of the wall and likely require different operating parameters for stable plasma operation. This is another indication for an immediate and urgent need for a better understanding of the effects of irradiation on retention properties of various materials.

For future fusion reactors that will produce neutrons in a steady-state operation, it is thought to produce ~ 20 dpa/year of neutron irradiation in the PFC wall. As the field and experiments move

towards steady-state operations, there will be a strong need for a database of material properties in a highly irradiated environment. The work in this study is a beginning to that database, but more importantly, proof that the DIONISOS experiment is well-suited and equipped to continue research along these lines.

Chapter 7

Conclusions

DIONISOS is a successful experiment demonstrating the ability to expose a target to a plasma while simultaneously irradiating with high energy ion beams. The hydrogenic trapping can be resolved into time-dependent concentration depth profiles. Fitting of these depth profiles can yield diffusion rates and integrating the depth profiles can lead to retention rates over the detection depth. DIONISOS can also directly measure effects of surface recombination. Over two years was spent designing, commissioning, and constructing this experiment as part of this thesis. DIONISOS has proven itself capable of performing all the dynamic experiments for which it was designed, and has even shown itself to be an important device in studying the effects of high-energy irradiation on hydrogenic retention. The success of this experimental facility is a major achievement for this thesis.

Experimental results from DIONISOS and modeling have conclusively shown that irradiation of a surface with high-energy ions greatly enhances the hydrogenic retention of the surface. The trap density produced by the irradiation increases as the 1/4-power of the dpa in the surface. This suggests a rapid approach to a saturation level, but saturation was not achieved up to a damage level of 1.75 dpa. It is likely that factors such as substrate material, irradiation temperature, irradiation ion/particle species, and irradiation ion/particle energy will also affect the relationship between trap production and surface damage in terms of dpa. Given the strong effect of irradiation on hydrogenic retention in Mo, a high priority should be given to the investigation of these dependencies in future studies.

DIONISOS results show hydrogenic retention in the first 5 μm of the surface is the highest for Mo temperatures of 400 K and 500 K and to lowest at 300 K. The low retention at 300 K is due to

the D being diffusion-limited to the first $\sim 1 \mu\text{m}$ of the surface and unable to reach the deeper traps caused by irradiation. The non-zero D concentrations at the end of range and the flat D/Mo depth profiles at elevated temperatures ($T_{mo} \geq 500 \text{ K}$) from the DIONISOS data imply that empty and D-filled trap sites are mobile and diffuse much deeper in the Mo than the $5 \mu\text{m}$ range of the NRA. This is confirmed by modeling and is an important result in understanding how the D inventory evolves over time in a Mo target. This also confirms that the hydrogenic retention in the first $5 \mu\text{m}$ of the surface for $T_{mo} \geq 500 \text{ K}$, is only a fraction of the total retention for the entire bulk.

While the hydrogenic retention is found to be independent of plasma ion energy, the surface recombination rate is found to increase with plasma ion energy. It is thought this is an effect of surface sputtering. Ion beam analysis and XPS results show a layer of impurities on the surface. As the plasma ion energy increases, the sputtering rate increases and the sputtered clean surface of the Mo has an increased rate of surface recombination. This is supported by the model in the respect that the D concentration depth profiles for the 350 eV/D+ plasma exposures were best fit if a reduced diffusion rate due to the low-Z impurities was removed and the pure Mo diffusion rates were used for the entire target.

The results from the Alcator C-Mod show that B contamination of Mo is related to reduced diffusion and strongly trapped D. In the $0.5 \mu\text{m}$ boron-rich layer, there was a D concentration of 0.007 D/Mo that can not be desorbed even with extended bakes at 720 K. The hydrogenic retention for the Alcator C-Mod tile was generally lower than for the pure Mo plate. This is due to the reduced diffusion in the boron-rich layer limiting the access of the solute D to the irradiation-produced traps in the bulk of the tile. It is not clear if the boron on the surface layer is collected locally or distributed evenly in the Mo. To gain a better understanding of the role of the boron in terms of hydrogenic retention, it must be determined if it is a global effect or an overlaying local effect.

Dynamically increasing temperature during a plasma exposure followed by rapid cooling when the plasma is removed, similar to what is found in tokamaks with inertially cooled walls, is shown to trap D deep in the surface. The increasing temperature allows the solute D, trapped D, and traps to diffuse into the bulk where they are "frozen" when the temperature rapidly returns to

~300 K. Modeling has shown the deeply trapped D to progress deeper into the bulk with each subsequent plasma/thermal cycle. This "ratcheting" of trapped D deep into the surface means the total hydrogenic retention of the target will not saturate until the entire depth has been filled.

There is strong evidence from both DIONISOS experimental data and modeling for plasma-produced trap sites that scale linearly with plasma flux density. It is hypothesized this is indication of a pressure-driven trap production mechanism. Any effect that scales with plasma flux density is of critical importance when extrapolating "laboratory" results to a tokamak situation where the plasma flux density can be orders of magnitude higher. The recipe for this effect appears to be high plasma flux density incident on a target with low natural hydrogenic solubility. This implies that this effect will not be as strong using a carbon or boron-coated PFC but will be apparent in the use of Mo or W PFC in tokamaks. This is supported by the high levels of hydrogenic retention seen in Alcator C-Mod during operation with "bare" Mo PFC. This conclusion is one of the most important of the thesis due to its impact on hydrogenic retention extrapolations to ITER and future reactors.

A 1-D, numerical, flux-conservation, slab model had been created based on experimental data and rates found on DIONISOS and physical arguments. This model re-creates the depth profiles and dynamic retention rates in the first 5 μm of the surface. The model is not fully developed and there is certainly room for expansion and refinement, but it has proved to be a valuable tool in recreating overall trends and magnitudes from the experimental data. The availability of a working model allows for rates, which are difficult or impossible to measure directly, to be isolated and solved for if all other unknowns can be determined through experimental results or literature.

The model has recreated the 0.35% linear dependence of D retention as compared to incident D ion fluence that was seen in the Alcator C-Mod experiments. This is mostly due to the application of an experimentally observed pressure-driven trap production mechanism that scales linearly with plasma flux density. The "ratcheting" of trapped D deeper into the tile bulk from repeated plasma exposures and thermal cycles also explains why there was no saturation seen in Alcator C-Mod. The model also recreated an ITER-like plasma discharge accounting for neutron irradiation of the PFC. The results for a simulated 300 s ITER-like discharge were hydrogenic retention rates of

$\sim 2.7 \times 10^{23}$ D/m² and trapped D as deep as 100 μ m into the surface. These results call into question the decision to use high-Z metal PFC in the divertor region of ITER.

Overall, a great deal about hydrogenic retention in an irradiated Mo surface has been revealed by the work on DIONISOS. Many issues and pre-conceptions in the field of plasma-surface interactions have been brought into question. However, the current thesis is only a small step towards the challenge of understanding the dynamics of plasma-surface interactions and the impact of irradiation on hydrogenic retention, and has only used a fraction of the capabilities of the DIONISOS experiment. Future work on DIONISOS will make major contributions towards understanding plasma-surface interactions in current tokamak devices and extrapolating to future fusion reactors.

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Appendix A: Flux and Particle Conservation Equations for Trap Model

The model is based on conservation of flux with an infinite particle sink boundary condition. This appendix will present the nomenclature and conservation equations used in the simulation in detail. The nomenclature is defined in the table at the end of this appendix.

The flux equations must be solved to determine the solute D, trapped D, and trap densities for each slab at each time step. Since some of the processes are only relevant in the surface (j=1) layer, the surface and the bulk must be calculated separately. The flux equations in the j=1 layer must use the reduced diffusion rates specific to the surface:

$$\phi_{Do,net} = \phi_{in} + D_{Do,surf} \cdot \nabla n_{Do,i-1,j=2,1}$$

$$\phi_{Dtr,net} = D_{Dtr,surf} \cdot \nabla n_{Dtr,i-1,j=1,2}$$

$$\phi_{tr,net} = D_{tr,surf} \cdot \nabla n_{tr,i-1,j=1,2}$$

The fluxes can then be used to determine the D and trap densities in the j=1 layer for each time step:

$$n_{Do,i,1} = n_{Do,i-1,1} + \left(\frac{\phi_{Do,net}}{\Delta z} - \frac{R \cdot (n_{Do,i-1,1})^2}{\Delta z} - T \cdot n_{Do,i-1,1} [n_{tr,i-1,1} - n_{Dtr,i-1,1}] \right. \\ \left. + \kappa \cdot n_{Dtr,i-1,1} + A_{trap} \cdot n_{Dtr,i-1,1} \right) \times \Delta t$$

$$n_{Dtr,i,1} = n_{Dtr,i-1,1} + \left(\frac{\phi_{Dtr,net}}{\Delta z} + \frac{R \cdot (n_{Do,i-1,1})^2}{\Delta z} + T \cdot n_{Do,i-1,1} [n_{tr,i-1,1} - n_{Dtr,i-1,1}] \right. \\ \left. - \kappa \cdot n_{Dtr,i-1,1} - A_{trap} \cdot n_{Dtr,i-1,1} \right) \times \Delta t$$

$$n_{tr,i,1} = n_{tr,i-1,1} + \left(\frac{\phi_{tr,net}}{\Delta z} - A_{trap} \cdot n_{Dtr,i-1,1} + \Omega_{plasma} + \Omega_{beam} \right) \times \Delta t$$

Note that filled traps can be annealed at the surface. The D trapped in annealed traps is assumed to go into solution in the surface layer. In the bulk layers (j≠1) surface processes such as surface recombination (R), trap annealing (A_{trap}), ion implantation (ϕ_{in}), and plasma-produced trap sites (Ω_{beam}), can be ignored. The flux equations in the bulk layers use the normal lattice diffusion rates:

$$\phi_{Do,net} = \phi_{in} + D_{Do} \cdot \nabla n_{Do,i-1,j=j+1,j} + D_{Do} \cdot \nabla n_{Do,i-1,j=j-1,j}$$

$$\phi_{Dtr,net} = D_{Dtr} \cdot \nabla n_{Dtr,i-1,j=j+1,j} + D_{Dtr} \cdot \nabla n_{Dtr,i-1,j=j-1,j}$$

$$\phi_{tr,net} = D_{tr} \cdot \nabla n_{tr,i-1,j=j+1,j} + D_{tr} \cdot \nabla n_{tr,i-1,j=j-1,j}$$

The fluxes can then be used to determine the D and trap densities in the j=1 layer for each time step:

$$n_{Do,i,j} = n_{Do,i-1,j} + \left(\frac{\phi_{Do,net}}{\Delta z} - T \cdot n_{Do,i-1,j} [n_{tr,i-1,j} - n_{Dtr,i-1,j}] + \kappa \cdot n_{Dtr,i-1,j} \right) \times \Delta t$$

$$n_{Dtr,i,j} = n_{Dtr,i-1,j} + \left(\frac{\phi_{Dtr,net}}{\Delta z} + T \cdot n_{Do,i-1,j} [n_{tr,i-1,j} - n_{Dtr,i-1,j}] - \kappa \cdot n_{Dtr,i-1,j} \right) \times \Delta t$$

$$n_{tr,i,j} = n_{tr,i-1,j} + \left(\frac{\phi_{tr,net}}{\Delta z} + \Omega_{beam} \right) \times \Delta t$$

These equations are solved for all slabs at each time step with the boundary condition that the final slab has all densities set to zero. Once all the slabs have been calculated the time step moves forward and the densities from the previous time-step are fed into the the new equations.

It should be noted that the second layer (j=2) will have slightly modified flux equations than the rest of the bulk layers since it has to compensate for the slower diffusion of D and traps from the surface layer.

Symbol	Definition
i	The index counter the time-steps (i.e. i=2 is the second time-step)
j	The index counter for the slabs (i.e. j=3 is the third slab)
Δt	Duration of each time-step [s]
Δz	Thickness of each slab [m]
ϕ_{in}	Incident plasma flux density [D/m ² s]
$\phi_{Do,net}$	Net flux density of solute D in (+) or out (-) of a slab [D/m ² s]
$\phi_{Dtr,net}$	Net flux density of trapped D in (+) or out (-) of a slab [D/m ² s]
$\phi_{tr,net}$	Net flux density of empty traps in (+) or out (-) of a slab [D/m ² s]
n_{Do}	Density of solute D in local slab [D/m ³]
n_{Dtr}	Density of trapped D in local slab [D/m ³]
n_{tr}	Density of traps in local slab [traps/m ³]
$D_{Do,surf}$	Diffusion rate of solute D in the surface layer (j=1) [m ² /s]
$D_{Dtr,surf}$	Diffusion rate of trapped D in the surface layer (j=1) [m ² /s]
$D_{tr,surf}$	Diffusion rate of traps in the surface layer (j=1) [m ² /s]
D_{Do}	Diffusion rate of solute D in all other layers (j≠1) [m ² /s]
D_{Dtr}	Diffusion rate of trapped D in all other layers (j≠1) [m ² /s]
D_{tr}	Diffusion rate of traps in all other layers (j≠1) [m ² /s]
R	Surface Recombination rate for solute D [s ⁻¹]
T	Rate at which solute D occupies available trap sites [s ⁻¹]
κ	Rate at which D is thermally de-trapped in the local slab [s ⁻¹]
A_{trap}	Rate at which traps are annealed from the surface layer (j=1) [s ⁻¹]
Ω_{plasma}	Plasma-induced trap production rate in the surface layer (j=1) [traps/m ³ s]
Ω_{beam}	Ion beam-induced trap production rate in the local slab [traps/m ³ s]