TRAPPING, DETRAPPING AND REPLACEMENT OF keV
HYDROGEN IMPLANTED INTO GRAPHITE⁺)

MASTER

J. Roth, B.M.U. Scherzer

Max-Planck-Institut für Plasmaphysik
EURATOM Association, D-8046 Garching
bei München, Federal Republic of Germany

R.S. Blewer, D.K. Brice, S.T. Picraux, W.R. Wampler

Sandia Laboratories⁺⁺)
Albuquerque, NM 87185, USA

ABSTRACT

Trapping and detrapping of low energy hydrogen isotopes in graphite is relevant to the collection of fuel particles in graphite probes for diagnostics of particle fluxes and energies in the plasma boundary layer, and to the recycling of fuel particles. The measurement of saturation concentrations by α profiling of D may be influenced by detrapping of deuterium by the analyzing ^3He -beam.

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Detrapping yields have been measured for 1 and 8 keV deuterium implanted to saturation concentrations in papyex and pyrolytic graphite at room temperature by 790 keV H^+ , 400 - 2500 keV $^3He^+$, and 400 - 1600 keV $^{14}N^+$ ions. Initial detrapping yields of 1 keV implanted deuterium by 790 keV $^3He^+$ and $^{14}N^+$ are 4 and 56 D-atoms/ion, respectively. The detrapping yield for $^{14}N^+$ -ions increases with increasing energy similar to the electronic stopping power of the ions indicating the influence of electronic excitation on the detrapping mechanism. Detrapping by 790 keV H^+ was found to be negligible. Papyex and pyrolytic graphite show similar behavior.

Careful determination of the deuterium saturation concentration from the D concentration profile by $D(^3He, \alpha)H$ nuclear reaction method and taking detrapping into account yields a value of 0.4 D-atoms/C-atom. Further, the replacement of hydrogen by deuterium at equal ranges (8 keV H^+ , 7 keV D^+) has been measured in pyrolytic graphite with elastic recoil detection (ERD) by 2.6 - 2.8 MeV 4He ions. The H/D isotopic replacement behavior in saturated layers is similar to that found in metals at low temperatures and in low-Z coatings as TiC at room temperature.

INTRODUCTION

Trapping of hydrogen isotopes with energies of several electron volts to several kilo electron volts in different types of graphite (pyrolytic, carbon paper, reactor graphite) and silicon has acquired considerable attention recently /1-5/ because of its usefulness as a diagnostic tool for the determination of particle fluxes and energy distributions in the boundary layer of magnetically confined fusion plasma experiments.

The choice of graphite or silicon as probe materials provides the advantage over most metals in that the hydrogen stopped in the probe is 100 % trapped and is immobile at room temperature up to a saturation concentration. Also this concentration is to a first approximation independent of the energy of the incident hydrogen ions. A further advantage is the absence of an oxide layer on C.

Nevertheless care must be taken in determining the trapped amount, usually given as an areal density (hydrogen-atoms/cm²) or as the concentration as a function of depth below the surface. Three different methods are commonly applied: a) thermal desorption, b) secondary ion mass spectrometry (SIMS), and c) high energy ion beam analysis by either nuclear reaction or particle scattering. The thermal desorption technique includes a number of different chemical species as H₂ and CH₄ evolving during heating.

This method and SIMS generally require independent calibration procedures. They will not be discussed here.

Nuclear reaction analyses have in the past yielded saturation concentrations in the same type of pyrolytic graphite which differ by about a factor of two /1, 2/. One possible reason for this discrepancy may be the detrapping effect by the analyzing high energy beams similar to that observed earlier for deuterium in BeO /6/.

In the present paper the detrapping cross sections of deuterium implanted to saturation into different types of graphite by H^+ , $^3H^+$ and $^{14}N^+$ -ions of various energies have been measured. By accounting for this cross section and for other effects as impurities and fluence measurement errors in the analyzing beam, as well as the influence of the implanted hydrogen on the electronic stopping power of the analyzing beam, a careful determination of the saturation concentration of deuterium in pyrolytic graphite has been made. Also the replacement efficiency for hydrogen saturated pyrolytic graphite samples by successive deuterium implantation of equal range has been measured and compared to the calculated value based on the measured hydrogen saturation concentration.

EXPERIMENT

The graphite samples were implanted at the Garching high flux ion source /7/ with a beam spot of 6.8 mm diameter over which the fluence is constant within 20 %. The current density was kept below 0.2 mA/cm^2 for all implantations. Thereby target heating by the implantation beam was generally kept below 30° centigrade except for those

samples investigated at Sandia/Albuquerque, in which the initial H-implant was below the room temperature saturation value because of beam target heating as will be discussed below. These samples were transferred in air to the analyzing devices. The detrapping measurements were performed at the 2.5 MeV accelerator in Garching using the $D(^3\text{He}, p)^4\text{He}$ nuclear reaction. Either the emerging protons were counted by a large angle detector situated at an angle of 135° to the incident beam or the α -particles were energy analyzed by a small angle detector at $\theta = 105^\circ$. The analyzing beam hit the target through a 1 mm diameter diaphragm situated a few cm in front of the target. The detrapping beams were also produced by the 2.5 MeV accelerator and passed through the same diaphragm. The analyzing energy of ^3He -ions was 790 keV. The integral of protons was calibrated against the α -particle integral at equal analyzing dose. The α -particle spectrum was transformed into a depth profile of deuterium concentration with the computer program LORI /17/ using nuclear reaction cross section data measured by Yarnell et al. /8,9/, electronic stopping power data compiled by Ziegler /13/, and measured values of analyzing beam dose times detector solid angle. The latter can also be obtained from the surface intensity of backscattered ^3He -ions from the graphite. The agreement is generally within a few percent. At high concentrations the contribution of implanted hydrogen to the electronic stopping powers gives a correction of the deuterium concentration calculated from the measured α -spectrum of $\lesssim 10\%$ and is taken into account.

The replacement coefficient was determined by successively implanting graphite samples first with 8 keV H^+ to saturation and then with 7 keV D^+ at equal range but with various fluences in the high flux source. These samples were also transferred in air to the 2.5 MeV accelerator for analysis. Additional to the nuclear reaction, elastic recoil detection-(ERD)-analysis was applied to these samples for simultaneous analysis of trapped areal densities of H and D using $\overset{\text{or } 2.8}{2.6} \text{ MeV } {}^4\text{He}^+$. Typical spectra of the nuclear reaction α -particles and elastic recoil protons and deuterons are shown in Fig. 1a and 1b. The depth resolution of the nuclear reaction is slightly superior to ERD, but on the other hand the ERD method is about a factor of 500 more sensitive than the nuclear reaction α profiling. The beam and detector geometries of both techniques are shown in the figure. A number of replacement measurements were also performed on samples which had been implanted to saturation with H in Garching and then with D at the Lintott accelerator at Sandia, Albuquerque. The analysis of these samples was performed at the 3 MeV accelerator at Sandia by using the ERD-method.

Material	Detrapping		Impl.	n_1	n_2	σ_1	σ_2
	Ions	Energy (keV)	Energy (keV)	(10^{17} D/cm ²)	(10^{17} D/cm ²)	(cm ²)	(cm ²)
papyex	H ⁺	790	1	2.39	-	$9.4 \cdot 10^{-20}$	-
"	³ He ⁺	790	1	0.55	1.8	$6.5 \cdot 10^{-17}$	$8.6 \cdot 10^{-19}$
"	¹⁴ N ⁺	400	1	1.06	1.34	$4.2 \cdot 10^{-16}$	0
"	"	790	1	1.18	1.12	$4.8 \cdot 10^{-16}$	0
"	"	1600	1	1.58	0.82	$5.6 \cdot 10^{-16}$	0
pyrol.graph.	³ He ⁺	400	1	1.81	-	$5.0 \cdot 10^{-18}$	-
"	"	790	1	2.0	-	$1.9 \cdot 10^{-18}$	-
"	"	2500	1	2.16	-	$9.4 \cdot 10^{-19}$	-
"	"	790	8	9.3	-	$2.9 \cdot 10^{-18}$	-
"	¹⁴ N ⁺	790	1	1.22	1.1	$6.1 \cdot 10^{-16}$	0
"	"	790	8	4.4	5.0	$5.48 \cdot 10^{-16}$	$2.8 \cdot 10^{-18}$

Table 1 Saturation areal densities and initial detrapping cross sections

RESULTS

The decrease of trapped deuterium areal density in initially saturated targets with fluence is shown in Fig. 2 for papyex and in Fig. 3 for pyrolytic graphite. Hydrogen, helium-3 and nitrogen ions were used for detrapping with energies between 400 and 2500 keV. Detrapping cross sections were determined from these curves by assuming a two-term inverse exponential decrease as used earlier for D in stainless steel /10/. Cross section data are listed in Table 1. The initial detrapping efficiency increases strongly with the atomic number of the incident ions. For hydrogen it is so small that it cannot with certainty be distinguished from the detrapping caused by the ^3He -beam used for analysis of the remaining deuterium. For helium and nitrogen bombardment of papyex the two components of the detrapping curves are clearly evident. The main difference between papyex and pyrolytic graphite seems to be the absence of a high initial detrapping cross section which is responsible for the detrapping of $\sim 10\%$ additional hydrogen that is trapped in papyex compared to pyrolytic graphite. In the case of N^+ σ_2 is so small that the amount of trapped deuterium becomes almost constant at a certain N^+ fluence.

Using these results, the saturation concentration of D in C was reinvestigated. The depth profile of an 8 keV D^+ implant with $5 \cdot 10^{18} \text{ D/cm}^2$ in pyrolytic graphite was determined by $\text{D}(^3\text{He}, \alpha)\text{H}$ nuclear reaction analysis.

The depth profile is shown in Fig. 4 corrected for the detrapping effect of the analyzing beam by extrapolation to zero analysing fluence, for a 1.6 % H_3^+ and HD^+ fraction in the analyzing beam, as measured by RBS on a Au-calibration sample, and by taking account of the increase in electronic stopping power of the He-ions in graphite due to implanted deuterium. A saturation concentration of (0.4 ± 0.06) D-atoms/C-atom was obtained.

The replacement of hydrogen implanted with 8 keV to saturation in pyrolytic graphite targets by subsequent 7 keV D^+ is shown in Fig. 5. The figure contains data measured at IPP and at Sandia. If both measurements are normalized to saturation there is reasonable agreement. The respective saturation values were $8.7 \cdot 10^{17}$ hydrogen atoms/cm² at IPP and $7.1 \cdot 10^{17}$ hydrogen atoms/cm² at Sandia. This discrepancy of 20 % may be due to different calibration procedures. Moreover the samples used at Sandia did not show initial deuterium saturation because of beam heating of the targets during implantation.

Fig.5 shows the isotope replacement behavior predicted by the local mixing model described in ref./18/. To compare the calculation with the data the retained H and D have been plotted normalized to the saturation areal density. However, using a saturation concentration of $n_{sat} = 0.4$ hydrogen atoms/C atoms and depth profiles from the TRIM code /19/ gives a saturation areal density which is smaller than either of the measured values, as the measured maximum penetration (fig.4) of 2.1×10^{18} C-atoms/cm² is 40 % greater than predicted by the TRIM code. This discrepancy is not understood

DISCUSSION

The mechanism of "detrapping" of implanted gas atoms in a solid by high energy ions with a range much larger than the depth of the implantation profile /6/ must clearly be distinguished from the "replacement" of a gas implant by ions of equal range /10-12/. Detrapping leads to an overall decrease in implant concentration while in a replacement experiment a saturation concentration is approximately conserved.

It is not yet understood which physical effect is responsible for detrapping. In a previous paper /6/ we have by comparing initial yields concluded that detrapping of implanted deuterium in BeO by beams of $^3\text{He}^+$ and H^+ is induced by electronic excitation rather than by nuclear collision cascades. In order to check this for the case of graphite we have compared the electronic stopping powers of $^3\text{He}^-$ and $^{14}\text{N}^-$ ions in carbon /13, 14/ with the initial detrapping cross sections of 1 keV D implants in graphite by $^3\text{He}^+$ and $^{14}\text{N}^+$ as a function of energy (Fig. 6). Although the stopping power and the detrapping cross sections show equal trends with increasing energy (increasing for $^{14}\text{N}^+$ and decreasing for $^3\text{He}^+$) in the range investigated, a much stronger increase with particle mass is observed for the detrapping cross section than for the electronic stopping power. The ratios of energy deposited in the implanted layer by $^3\text{He}^+$ and $^{14}\text{N}^+$ of equal energy are similar for nuclear and electronic stopping in graphite, but the nuclear stopping power of $^{14}\text{N}^+$ in C decreases with

energy for $E > 10$ keV while the detrapping cross section increases for $E > 400$ keV. We therefore believe that detrapping is more likely due to electronic excitation than to nuclear collisions. Apparently the detrapping mechanism is nonlinear with energy deposition in the target similar to effects found in particle track registration /15, 16/.

The replacement behavior of 8 keV H^+ by 7 keV D^+ in pyrolytic graphite (Fig. 5) is in good agreement with a pure mixing law /11/ providing the depth dependence of this effect is taken into account /18/.

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FIGURE CAPTIONS

- Fig. 1a Energy distribution of particles from the $D(^3\text{He}, \alpha)H$ nuclear reaction and backscattered ^3He atoms obtained by analyzing a C target implanted with H and D with 790 keV ^3He .
- Fig. 1b Energy distribution of recoil H and D atoms obtained by analyzing a C target implanted with H and D with 2.6 MeV ^4He . The forward-scattered ^4He atoms are stopped in a 5 μm stainless steel foil in front of the detector.
- Fig. 2 Retained deuterium implanted to saturation into PAPYEX at 1 and 8 keV as a function of H, He and N fluence
(o, x, Δ) measured values
(—) two component exponential dependence
- Fig. 3 Retained deuterium implanted to saturation into pyrolytic graphite at 1 and 8 keV as a function of He and N fluence
($\square$, x, $\bullet$, o) measured values
(—) two component exponential dependence

Fig. 4 Depth profile of 8 keV D^+ implanted into pyrolytic graphite to saturation ($5 \cdot 10^{18} \text{ D/cm}^2$), taken by $D(^3\text{He}, \alpha)H$ nuclear reaction analysis with 790 keV $^3\text{He}^+$. Corrections have been made for a) detrapping, b) impurities in the analyzing beam, c) electronic stopping power of implanted deuterium.

Fig. 5 Decrease of trapped amount of H, n_H and increase of D, n_D , in pyrolytic graphite during 7 keV D implantation following a preimplantation of $5 \cdot 10^{18} \text{ H/cm}^2$ at 8 keV. The trapped amounts are normalized to the amount trapped in saturation n_s . The dashed and solid lines are the calculated curves using the local mixing model /18/.

Fig. 6 Detrapping cross sections of 1 keV D^+ implanted in PAPHYEX by $^{14}\text{N}^+$ -bombardment and in pyrolytic graphite by $^3\text{He}^+$ bombardment as a function of detrapping energy. For comparison the respective electronic stopping powers /13, 14/ are included.

Fig. 1a

Fig. 1b

Fig. 2

Fig. 3

8 keV D⁺ → pyrol. graphit.

Fig. 1