CONF-740104--8

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INTERACTIONS WITH INSULATOR AND METAL SURFACES

by

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Presented at:

Conference on Surface Effects in Thermonuclear
Devices and Reactors,
Argonne National Laboratory, January 10-12, 1974

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CHEMICAL EFFECTS OF THERMONUCLEAR PLASMA INTERACTIONS WITH INSULATOR AND METAL SURFACES*

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Abstract

Deuterium and tritium, as well as plasma impurities such as oxygen and nitrogen ions, are chemically reactive particles in contradistinction to helium ions.

The interactions of chemically reactive ions with insulator and metal surfaces result in specific chemical effects which must be considered in sputtering, blistering, trapping and re-emission processes involving these projectiles. Chemical sputtering and chemical trapping of ion beam flux are examples of chemical interaction effects which are discussed.

Bombardment of a niobium surface by oxygen and nitrogen ions results in the formation of sputtered niobium oxide and nitride molecules. The molecular species are identified and characterized by means of their vibrational spectra using isotopic substitution and matrix isolation techniques. Results using matrix isolation spectroscopy for both physical and chemical sputtering studies on materials of CTR interest are presented.

Chemical trapping is evaluated as a method of chemically pumping the major fraction of the ion beam flux in the divertor of next generation Tokamaks. Suitable trapping surfaces, surface lifetimes, and reprocessing schemes are discussed on the basis of available information on trapping efficiencies and thermochemical data for a variety of metals.

Introduction

In contradistinction to noble gas ions, D^+ and T^+ are reactive particles whose interactions with insulator surfaces such as metal oxides or nitrides result in chemical reactions leading to a variety of sputtered products as well as surface compounds. The effects of such interactions can have serious consequences for the performance of insulators. For example, reduction of surface and subsurface layers to lower oxides and possibly to metal can, in principle, degrade insulating properties below acceptable levels.

Because of the paucity of quantitative work in this area, the seriousness of these effects for the performance of insulators in CTR applications remains to be assessed.

Sputtered molecules or molecular fragments which are ejected from a surface as the result of high energy collisions often involve novel or poorly characterized chemical species. Furthermore, such species have only a transitory existence under ordinary, ambient conditions of temperature and pressure. A major technique that has been employed up to now to study the nature of sputtered products has been mass-spectroscopy. A variety of important characteristics of molecules and molecular fragments, however, are not amenable to study by means of this dynamic technique. For this reason, matrix isolation spectroscopy has been developed by us as a sensitive new method to study the chemical sputtering process (1, 2).

Although there is a wealth of information about reactions of hydrogen with a wide variety of metals, the data relate almost exclusively to conditions at thermodynamic equilibrium (3). In a fusion reactor where the average particle energies are of the order of 10 Kev, pulsed modes of operation are contemplated and temperature gradients of 10^6 °K/meter can occur, data obtained at thermodynamic equilibrium can at most be expected to furnish guidelines for the many "chemical" parameters such as the nature of compounds formed, the kinetics of reactions, the rates of diffusion, the heats of adsorption and desorption, which are characteristic of an operating fusion reactor.

The processing of large volume of D^+ and T^+ , after removal from the reactor, at thermal energies, and the chemical consequences of energetic particle interactions with reactor components such as the first wall, are of prime importance insofar as tritium holdup and release through permeation are concerned. The concentration of tritium in the plasma will depend in part on the rate of permeation through the first wall, and this rate may change in both magnitude and direction during the transient conditions associated with bringing the plasma to the desired steady state (or periodically pulsed) operating conditions.

A particular area of work included in the scope of the present discussion is ion beam flux trapping or "chemical pumping" at metal surfaces. The aim of work in this area is directed at achieving a better understanding of the trapping process to aid in defining a set of conditions for markedly increasing the total trapped ion beam flux per cm^2 of metal surface (4).

The Application of Matrix Isolation Spectroscopy to Quantitative Sputtering Studies

A. Sputtered Metal Atoms

Matrix isolation is a technique for capturing and immobilizing transient or reactive species in an inert, usually a noble gas matrix by codeposition on a cold surface. After deposition, the reactive species are prevented from reacting with each other by bimolecular collisions because the matrix temperature is too low to allow diffusion to occur. Furthermore, the energy remaining to the reactive species is too small to lead to unimolecular decomposition. As a result, sufficient numbers of sputtered atoms or molecules can be collected in a matrix to provide a sample large enough for spectroscopic examination.

Because the matrix isolation method for measuring sputtering yields does not require a weight loss determination of the target material, it is of particular interest for establishing D^+ and T^+ sputtering yields of metals such as Nb, V, Ti and Zr which tend to absorb and retain the bombarding projectiles, thus in fact experiencing a weight gain during bombardment (5). The sensitivity of the method for the detection of metal atoms has already been developed to the extent that a quantity of sputtered atoms equivalent to 0.1 monolayer can be determined with good accuracy. Improvements in sensitivity by two orders of magnitude can be expected (1).

The process of sputtering and of sputtered atom collection take place within the evacuated target-collector assembly illustrated in Fig. 1. The main dewar body is designated by "a". A closed-cycle He refrigerator is attached to a flange (not shown) at the top of the dewar. A copper sample block, indicated by "b", is mounted directly to the second stage of the refrigerator. This block has provision for mounting a one inch diameter sodium chloride plate, "f", which is cooled to 14°K during refrigerator operation. The salt plate has a 0.25 inch diameter hole through its center which geometrically defines the mass and energy selected ion beam and allows it to strike the target. A copper radiation shield, "d", is attached to the first stage of the refrigerator and surrounds the sample block. Suitable openings are provided for the entering ion beam and the target assembly. The hollow stainless steel tube, "c", serves a dual purpose. It supports the target and provides a means of conducting the matrix gas into the dewar. The hollow brass target holder, "e", has the appropriate metal foil targets mounted on its face. Six 0.0156 inch holes

circularly surround the target and direct the matrix gas toward the salt plate during matrix deposition. The target holder is electrically insulated from the rest of the system by means of a threaded, hollow nylon rod between a block at the base of the stainless tube and the brass holder. A thin insulated wire passes from the target holder to a current measuring circuit through a vacuum feedthrough at the top of the dewar. Thus, the positive ion current arriving at the target during bombardment can be measured. The independently grounded beam-defining aperture, "g", is placed in front of the salt plate assembly to limit the diameter of the incoming ion beam (indicated by the hatched arrow) to the 0.25 inch hole in the salt plate.

The back-sputtered metal atoms mix with an excess of noble-gas matrix atoms in a ratio of $\sim 1:10^3$ and codeposit on the salt plate at $\sim 14^\circ\text{K}$. At the conclusion of the bombardment the target assembly is rotated to a position outside the radiation shield. Then the entire flange-mounted refrigerator-sample assembly is rotated 90° to allow spectroscopic measurements to be made through the dewar windows.

The absorption spectra of Au atoms in Ar, Kr and Xe matrices are shown in Fig. 2. The spectra of Ti (6), Nb (2), and Mo (7) atoms in Ar matrices are shown in Fig. 3. Each atomic species displays a characteristic matrix spectrum which can be correlated with the spectrum of the free gaseous atom.

Sputtering yields are calculated using the equation

$$S = \frac{1.158 \times 10^{-4} \times A_\sigma \times a_s}{f_{lu}^{(m)} \times G \times C \times I \times t}$$

where

A_σ = integrated absorbance over an absorption band

a_s = the area of the salt plate sampled by the spectrometer beam

$f_{lu}^{(m)}$ = oscillator strength (in the matrix) of the atomic transition

G = geometric factor, calculated assuming a cosine distribution of sputtered products

C = sticking coefficient

$I \times t$ = integrated ion beam current to the target

Results already obtained on sputtering yield determinations of Au and Nb indicate that continued development of the matrix technique will provide a rapid and sensitive new method for measurements of this kind.

B. Chemical Sputtering

Bombardment of a Nb metal target with oxygen and nitrogen ions results in addition to sputtered Nb metal atoms, in the ejection of NbO and NbN molecules respectively. The molecular sputtered products were identified by means of their infrared spectra using isotopic substitution techniques. Table I reports the observed frequencies for Nb¹⁶O and Nb¹⁸O and the observed and calculated ρ values:

$$\rho_{\text{obs}} = \nu(\text{Nb}^{18}\text{O})/\nu(\text{Nb}^{16}\text{O}), \quad \rho_{\text{calc}} = [\mu(\text{Nb}^{16}\text{O})/\mu(\text{Nb}^{18}\text{O})]^{1/2}.$$

ν is the observed frequency and μ is the reduced mass (8).

The uncertainty in frequency measurements (less than 1.0 cm⁻¹) leads to an uncertainty of less than 0.0010 in ρ_{obs} ; the anharmonic correction to an uncertainty of less than 0.0004. The agreement of ρ_{obs} and ρ_{calc} in Table I confirms the assignment to NbO. Furthermore, no additional features were observed in a mixed ¹⁸O₂/¹⁶O₂ experiment eliminating the possibility that the absorber contains more than one equivalent O atom. Agreement with the observed gas phase $\Delta G_{1/2}$ (981.37 cm⁻¹) of the ⁴ Σ^- state is good taking account of the expected matrix shift. The origin of the observed triplet structure for Nb¹⁶O and Nb¹⁸O is likely multiple stable matrix sites.

TABLE I
Observed Frequencies of Nb¹⁶O and Nb¹⁸O Isolated in
an Ar Matrix at 14°K with Observed and Calculated ρ Values

Nb ¹⁶ O	Nb ¹⁸ O	ρ	
obs $\Delta G_{1/2}$	obs $\Delta G_{1/2}$	obs	calc
(cm ⁻¹)	(cm ⁻¹)		
964	918	0.952 ₃	0.9513
968	921	0.951 ₄	0.9513
971	924	0.951 ₆	0.9513

TABLE II
Observed Frequencies of Nb¹⁴N and Nb¹⁵N Isolated in
an Ar Matrix at 14°K with Observed and Calculated ρ Values

Nb ¹⁴ N	Nb ¹⁵ N	ρ	
obs $\Delta G_{1/2}$	obs $\Delta G_{1/2}$	obs	calc
(cm ⁻¹)	(cm ⁻¹)		
1002.5	974	0.971 ₆	0.9707

Partial analysis of the visible spectra of Nb^{16}O and Nb^{18}O has shown a v' progression (0-0 through 3-0) of an electronic transition with average $\Delta G'_{1/2}(\text{Nb}^{16}\text{O}) = 894$ and $\Delta G'_{1/2}(\text{Nb}^{18}\text{O}) = 894 \text{ cm}^{-1}$. The value of $\rho_{\text{obs}} = 0.9497$ is in satisfactory agreement with $\rho_{\text{calc}} = 0.9513$. The band origin for Nb^{16}O is about $15\,364 \text{ cm}^{-1}$ (650.7 nm). The band origin and vibrational spacing are in agreement with gas phase values for the $^4\Pi-^4\Sigma^-$ transition. Additional bands in this spectral region have not been fully analyzed, but the present data support the assignment of a $^4\Sigma^-$ electronic ground state for NbO .

Table II reports the results for Nb^{14}N and Nb^{15}N . The agreement of calculated and observed ρ values is within experimental uncertainties. No additional features were observed in a mixed $^{14}\text{N}_2/^{15}\text{N}_2$ experiment.

Study of the other observed ir absorption of Nb-O_2 species as well as the visible spectrum of both NbO and NbN is in progress.

The Mechanism of Chemical Trapping of Deuterium in Metals

Among the chemical effects of energetic plasma particle interactions with metals, the trapping of D^+ and T^+ by certain metals can potentially be an extremely useful phenomenon for pumping and processing the thermonuclear fuel.

To gain an appreciation of the magnitude of the problems associated with plasma processing in a full-scale fusion reactor, a consideration of the relevant design parameters is in order. For the purposes of this discussion, consider a toroidal D-T reactor with total thermal fusion power of 5500 MW achieved by the fusion of 0.0023 moles of DT/second (9). The daily fuel consumption in the plasma is 0.39 kg D and 0.575 kg T while the production of He^4 is 0.77 kg. For reasonable fuel burnup (3.9%), it turns out that close to 0.1 mole or $\sim 6 \times 10^{22}$ plasma particles (D^+ , T^+ , He^+) must be removed from the reactor every second. An equal number of D and T particles must, of course, be reinjected into the reactor every second to provide new fuel. To handle this amount of gas at thermal energies in conventional vacuum systems requires a throughput of $\sim 3000 \text{ torr liter/sec}$. In turn, to maintain a base pressure of 10^{-5} torr , a pumping speed of 10^9 liters/sec is required. These numbers indicate the magnitude of the vacuum pumping problem for a gas at thermal energies. However, the particles arrive in the divertor region with their full plasma kinetic energy. They must therefore be slowed down and thermalized before they can be handled in conventional systems of whatever size as thermal gas.

If the incoming D^+ and T^+ ions could be immediately trapped when first striking a surface in the divertor, pumping speed requirements would be reduced by a factor of 20 assuming 5% burnup and zero trapping of He^+ .

Studies of deuterium trapping in solid targets have shown its dependence both on bombardment time and target temperature (10).

These results can be understood on the basis of the following considerations. After slowing to thermal energies, the ions diffuse through the solid lattice but on reaching the surface encounter a potential barrier inhibiting their escape due to the heat of solution of deuterium in the metal. The escape probability is given by $e^{-Q/RT}$ where Q is the heat of solution. The "trapped" deuterium will be able to diffuse through the lattice without being able to escape from the surface over a certain temperature range because the activation energies for diffusion are much lower, ~ 5 kcal/mole, than the heats of solution, 20-60 kcal/mole. The decreasing trapping efficiencies at higher temperatures are due to the increasing probability of the diffusing D atoms to overcome the potential barrier for escape from the surface. Furthermore, it appears that as the surface layers are converted to a bulk deuteride (or tritide) phase, no further uptake of deuterium occurs. The elucidation of this rejection phenomenon is of fundamental importance to an understanding of the trapping mechanism and therefore to the ultimate practical utilization of trapping as a means of handling thermonuclear plasmas. The chemical sputtering studies described above are being extended to shed light on various aspects of the chemical trapping mechanism.

Although materials development and a more detailed knowledge of the trapping process will undoubtedly allow one to trap larger numbers of D and T particles per cm^2 than current experiments would indicate, we will use the number 10^{21} particles/ cm^2 to calculate the exposure time of a trapping surface (11). With 6×10^{22} particles leaving the reactor per second and a trapping surface area of $5 \times 10^5 cm^2$, the surface would have to be renewed every 8300 seconds. If the surface were that of a continuously moving strip of Ti metal 20 cm in width and $2.5 \times 10^4 cm$ long, its velocity would have to be 3 cm/sec. One mole of TiD_2 (TiT_2) would be produced every 10 seconds leading to a total production rate of 200 kg per day. If the total thickness of the Ti strip is 1 mm, a layer 0.1 mm thick will be converted to TiD_2 (TiT_2). About two tons of Ti would have to be processed each day to recover the D and T.

The above discussion illustrates that the unprecedented fluences of energetic D^+ , T^+ and He^+ to which trapping surfaces are exposed in the divertor region of a toroidal fusion reactor present a series of problems each of which must be studied in detail before a realistic appraisal of the feasibility of this technique for plasma handling can be fully evaluated.

References

*Work performed under the auspices of the U. S. Atomic Energy Commission.

1. D. M. Gruen, S. L. Gaudioso, R. L. McBeth and J. L. Lerner, J. Chem. Phys., In Press.
2. D. W. Green, D. M. Gruen, F. Schreiner and J. L. Lerner, Applied Spectroscopy, In Press.
3. "Metal Hydrides", W. M. Mueller, J. P. Blackledge and G. G. Libowitz, editors, Academic Press, New York (1968).
4. D. M. Gruen in "The Chemistry of Fusion Technology", D. M. Gruen, editor, Plenum Press, New York (1972).
5. A. J. Summers, N. J. Freeman and N. R. Daly, Paper 4.1, B.N.E.S. Nuclear Fusion Reactor Conf., Culham, England (1969).
6. D. M. Gruen and D. H. W. Carstens, J. Chem. Phys. 54, 5206 (1971).
7. D. W. Green and D. M. Gruen, J. Chem. Phys., In Press.
8. D. W. Green, W. Korfmacher and D. M. Gruen, J. Chem. Phys. 58, 404 (1973).
9. E. F. Johnson in "The Chemistry of Fusion Technology", D. M. Gruen, editor, Plenum Press, New York (1972).
10. G. M. McCracken and S. K. Erents, Paper 4.2, B.N.E.S. Nuclear Fusion Reactor Conf., Culham, England (1969).
11. O. C. Yonts and R. A. Strehlow, J. Appl. Phys. 33, 2903 (1962).

Fig. 1. Sputtering target-matrix isolation assembly

Fig. 2. Resonance transitions of Au atoms isolated in Ar, Kr and Xe matrices at 14°K.

Fig. 3. Absorption spectra of Mo atoms (top), Nb atoms (middle), Ti atoms (bottom) in Ar matrices at 14°K.

3. Absorption spectra of Mo atoms (top), Nb atoms (middle), Ti atoms (bottom) in Ar matrices at 14°K.