

SATURATION AND ISOTOPIC REPLACEMENT OF DEUTERIUM
IN LOW-Z MATERIALS*

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Abstract

MASTER

The saturation and replacement of hydrogen isotopes implanted into TiC, TiB₂, VB₂, B₄C, B, Si, and C has been examined experimentally and modeled theoretically. The deuterium saturation concentrations for these materials varied from .16 to .57. A new isotopic replacement model is presented which predicts isotopic trapping and exchange on the basis of the depth dependence of the implanted ions and the experimentally determined hydrogen saturation concentrations. Our results indicate that, for these materials used as coatings on components in a D-T fueled tokamak, T recovery by ion induced replacement with H or D should be feasible and that T buildup will be at tolerable levels.

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1. INTRODUCTION

A more complete understanding of the complicated processes which occur at the plasma-wall boundary is required with the approach of the D-T burning tokamak era. This is particularly true if T-inventories and D-T fuel ratios are to be controlled in future devices such as TFTR, ETF, and INTOR. For example, there is currently a great concern that, because of the limited amount of T allocated to TFTR,¹ the demonstration of break-even may be jeopardized. Also, the T-purity of the plasma in a two-component tokamak such as TFTR may be compromised because of the isotope exchange effect.²

The present experiments determine the saturation and isotopic replacement of hydrogen implanted into the low-Z materials, C, Si, B_4C , TiC, VB_2 , TiB_2 , and B. The main benefit of utilizing these low-Z materials in a tokamak³ is the reduction of the plasma's Z_{eff} and the corresponding increase in core temperature. Although some of the samples were in bulk form (e.g., carbon), many were in the form of thin coatings (e.g., titanium di-boride on graphite) and were part of the TFTR Flexibility Modification (TFM) program. The aim of FTM is to screen candidate low-Z coating materials for use in TFTR. Along with the demanding structural requirements,⁴ the hydrogen (especially T) recycling and buildup potential of each candidate are important factors to be considered in choosing suitable coating materials for components such as limiters or liners in tokamaks.

We also report a new model to describe hydrogen isotope replacement. Our model includes the initial depth distributions of the implanted species and uses only one experimentally measurable parameter, namely the saturation hydrogen concentration, which is specific to the target material and dependent only on temperature. This model gives excellent agreement with new data reported here and with previously reported data for stainless steel.

In the final section of this paper, this model has been used to predict T buildup and recovery characteristics when these materials are exposed to actual tokamak plasma conditions (i.e., incident ions with Maxwellian energy and isotropic angular distributions).

2. EXPERIMENTAL

The hydrogen retention and replacement properties of the materials were studied by implanting H or D at an energy of 1.5 keV/ion, chosen to correspond to the upper end of typical particle energies at the plasma edge. At these energies little or no blistering is anticipated.⁵ All implants were carried out at ambient temperatures. The beam uniformity was measured by implanting low fluences of D into C (papyex) and measuring the lateral distribution of retained D using $D(^3\text{He},p)$ analysis with 700 keV ^3He ions. The resulting fluence uniformity was $\sim \pm 10\%$. The flux of the beam was maintained < 60 particle $\mu\text{A}/\text{cm}^2$ so that the power delivered to the target was < 100 mW/ cm^2 . The analysis beam delivered approximately the same power flux. Although the sample temperature was not monitored, we believe that, because of the low power deposited, the target temperature never exceeds $\sim 50^\circ\text{C}$. The TiC , B, and TiB_2 were formed by chemical vapor deposition on graphite substrates; the VB_2 was made by borodizing vanadium; and the B_4C was hot pressed and in bulk form. The reference materials were carbon (pyrolytic graphite and papyex) and single crystal silicon.

The total amount of H or D retained within ~ 500 nm of the surface was monitored as a function of incident fluence using $D(^3\text{He},p)$ nuclear reaction analysis (NRA) for D, and $H(^{19}\text{F},\alpha\gamma)$ resonant nuclear reaction analysis (RNRA) profiling for H. Elastic Recoil Detection (ERD) was used in some cases to

simultaneously measure the total amounts of H and D.^{6,7} The concentration depth profiles of H measured by RNRA were performed utilizing beams of ~ 7 MeV ^{19}F .

In the materials we examined, it was found that at low fluences ($< 10^{16} \text{ cm}^{-2}$) all the incident H, or D, was retained in the sample, apart from a small fraction (typically 5-10%) which was kinematically reflected.⁸ Depth profiling showed that the hydrogen was retained at the end of its implant trajectory in the material and therefore the deposition probability is totally determined by the range and straggling of the hydrogen, both of which can be theoretically predicted. This immobility of implanted hydrogen is found in many non hydride-forming materials at temperatures where normal diffusion is suppressed.

As the incident fluence was increased, a maximum hydrogen concentration (saturation) was eventually reached in each of these materials. To characterize the isotopic exchange behavior we implanted the D saturated candidate materials with H and monitored the D and H content of the samples as the H displaced the D.

3. THEORY

We have found that for projectile energies in the range 0.5 to 14 keV both the saturation behavior and the isotopic exchange process can be described by a simple macroscopic model.⁹ The model has as its single characteristic parameter the atomic density of hydrogen at saturation, N_g , which can be experimentally measured. The saturation concentration is a material characteristic and will depend on temperature but only room temperature values are examined here.

We now describe the model in some detail. Let $d\phi_1(t)/dt$ and $d\phi_2(t)/dt$ be the fluxes of isotopes 1 and 2 respectively as functions of time t . We define the respective local atomic concentrations as $N_1(x,t)$ and $N_2(x,t)$, where x is the depth into the target. Finally, we let $P_1(E_1,x)dx$ and $P_2(E_2,x)dx$ be the probabilities that isotopes 1 and 2 will come to rest in the depth interval $(x, x + dx)$ after having been incident on the target surface with energies E_1 and E_2 , respectively.

Our model treats the saturation and isotopic exchange processes differentially in the depth variable x . That is, it is assumed that at a depth where saturation has not been reached, i.e., $N_1 + N_2 < N_g$, the incident particles are trapped near the end of their trajectory so that

$$\frac{dN_1(x,t)}{dt} = P_1(E_1,x) \frac{d\phi_1}{dt} \quad (1a)$$

$$\frac{dN_2(x,t)}{dt} = P_2(E_2,x) \frac{d\phi_2}{dt} \quad (1b)$$

Thus, as long as the local concentration is below saturation we have

$$N_1(x,t) = \phi_1 P_1(E_1, x) \quad (2a)$$

$$N_2(x,t) = \phi_2 P_2(E_2, x) \quad (2b)$$

This behavior implies: 1) a high probability that a hydrogen ion coming to rest near an unoccupied trap will be captured by the trap, and; 2) a high probability for re-capture by a trap should a hydrogen atom be dislodged by a subsequently implanted projectile.

When saturation is reached additional hydrogen coming to rest in the region will find no available sites unless some of the previously trapped hydrogen is detrapped. It is assumed in our model that a hydrogen atom coming to rest in an already saturated region competes on an equal basis with the local hydrogen atoms already present for the available trap sites and that the single atom which does not find a trap is then lost from the material. The above description of the trapping behavior in a saturated region, (i.e., $N_1 + N_2 = N_s$) leads to the mathematical description

$$\frac{dN_1(x,t)}{dt} = \frac{N_2}{N_s} P_1(E_1, x) \frac{d\phi_1}{dt} - \frac{N_1}{N_s} P_2(E_2, x) \frac{d\phi_2}{dt} \quad (3a)$$

$$\frac{dN_2}{dt} = - \frac{dN_1}{dt} \quad (3b)$$

The first term on the right of Eq. (3a) gives the rate for projectiles of type 1 to replace isotopes of type 2 in the region while the second term gives the rate for projectiles of type 2 to replace isotopes of type 1 in the region. Thus, since $N_1 + N_2 = N_s$, we may solve 3a to yield

$$N_1(x,t) = \left\{ N_1(x,0) + \int_0^t dt P_1(E_1,x) \frac{d\phi_1}{dt} e^{[\phi_1(\tau)P_1 + \phi_2(\tau)P_2 - N_s]N_s} \right\} x e^{-[\phi_1(t)P_1 + \phi_2(t)P_2 - N_s]N_s} \quad (4a)$$

$$N_2(x,t) = N_s - N_1(x,t) \quad (4b)$$

where it is assumed that at $t = 0$, $\phi_1(0)P_1 + \phi_2(0)P_2 = N_s$. That is, the local region has been brought to saturation by $t = 0$.

The expression in (4a) is quite complicated and shows that the local concentrations are not simple functions of ϕ_1 or ϕ_2 , but depend sensitively on the history of the implantation sequence through the integral on the right hand side. Most experiments, including those reported here, are carried out by implanting one isotope of hydrogen after which the second type is implanted in order to study the replacement mechanism. Under these conditions, if isotope 1 is the first implanted, then $d\phi_1/dt$ is zero during the time of the second implant and the equation simplifies considerably. For this implantation scenario we thus have during the first implant

$$N_1(x,t) = \begin{cases} \phi_1(t)P_1(E_1,x) & \text{for } \phi_1(t)P_1(E_1,x) < N_s \\ N_s & \text{for } \phi_1(t)P_1(E_1,x) \geq N_s \end{cases} \quad (5a)$$

and

$$N_2(x,t) = 0 \quad . \quad (5b)$$

Then during the second implant, which is assumed to start at t_1 ,

$$N_1(x,t) = N_1(x,t_1) \quad (6a)$$

and

$$N_2(x,t) = \phi_2(t)P_2(E_2,x) \quad (6b)$$

as long as $N_1(x,t_1) + \phi_2(t)P_2(E_2,x) < N_s$. When saturation is reached at x , i.e., at times t such that $N_1(x,t_1) + \phi_2(t)P_1(E_2,x) > N_s$, then the behavior is described by

$$N_1(x,t) = N_1(x,t_1) \exp\left(-\frac{\phi_2(t)P_2(E_2,x) + N_1(x,t_1) - N_s}{N_s}\right) \quad (7a)$$

$$N_2(x,t) = N_s - N_1 \quad . \quad (7b)$$

Thus, Eqs. (5a,b) are used to describe the saturation behavior of the first implant, while Eqs. (6a,b) and (7a,b) are used to describe the isotopic replacement process. The saturation concentration, N_s , and the depth distribution functions P_1 and P_2 are needed in order to compare these equations to experiment. Theoretical areal densities are obtained from Eqs. 5-7 by integration over x . The important features of our model are shown in Fig. 1 where calculated D profiles for the buildup to saturation and subsequent replacement by H are plotted. We have observed the predicted double peaking of replacement profiles in measurements of D:H exchange in Si where our depth resolution was sufficient to permit studies of the depth distribution.

The saturation concentration, N_g , is obtained here by fitting the theory to experimental data, although this parameter can be directly measured by other means. The depth distribution functions P_1 and P_2 can be determined from standard transport theory. It should be pointed out that the precise value obtained for N_g through our fitting procedure is slightly dependent on the form assumed for these functions. In order to determine the sensitivity of the fitted N_g values to the choice of functions, we have utilized a variety of functional forms for P_1 and P_2 with range and straggling parameters as obtained from transport theory calculations. We find that, in general, changing the form of P_1 and P_2 results in changes to N_g of less than 10%. As a result, we have adopted a standard form for these functions which is a beta-distribution with parameters as determined by Monte Carlo calculations with the TRIM code.¹⁰

4. RESULTS AND DISCUSSION

4.1 Mono-Energetic Implants

The study of hydrogen retention and isotopic replacement in materials exposed to energetic hydrogen ions has recently received much attention¹¹⁻¹⁹ largely due to the importance of these processes on the buildup and recycling of H isotopes. The saturation curves for 1.5 keV D implants into the materials of this study are shown in Fig. 2. All of the materials behave similarly, but have different saturation concentrations. Using Eq. (5a) the saturation concentrations N_s for each material were determined from fits to the data. Table I summarizes the parameters used to model saturation in these materials. This table gives the saturation concentrations in units of D/cm^3 and D/host atom ratio, as well as the range and straggling parameters and the saturation areal densities for 1.5 keV D in the various materials (estimated accuracy of these values is $\pm 10\%$). The 2.5×10^{22} D/cm³ saturation value for Si is in reasonable agreement with direct measurements of 2.0×10^{22} .

Blewer, et al.¹¹ recently reported isotopic replacement of deuterium implanted into 316 stainless steel at $-120^\circ C$ by subsequent implantation with hydrogen. They used a model to describe the replacement which involved two energy dependent replacement cross sections corresponding to two different types of trapped hydrogen. Figure 3 shows a comparison of the present theory with these data for stainless steel. The retained D versus D plus H fluence is shown in the figure. The left-hand

portion of each curve (saturation curve) represents the D implant while the right-hand portion of each curve (isotopic exchange curve) represents the H implant. The solid curves are the predictions of the model described above using a value for N_g equal to the target atomic density. The excellent agreement between the model and experiment shows that our model predicts the correct energy dependence of the isotopic replacement process.

This agreement is also characteristic of the fits obtained for the bulk and coating materials studied. For example, Fig. 4 shows theory and data for 1.5 keV D-H saturation-replacement in pyrolytic graphite and TiC. The amounts of retained D and H were simultaneously monitored by 2.6 MeV ^4He ERD⁷ for the graphite data.

It should be pointed out that the saturation value we measure for H in carbon (both papyex and pyrolytic graphite) is $.53 \pm .05$. This value is considerably higher than that reported by Cohen and McCracken (.32) and Scherzer, et al.²¹ (.30), and is in much better agreement with the results of Langley, et al.¹⁶ (.63), Roth, et al.²² (.40), and Staudenmaier, et al.¹⁸ (.50). At present the discrepancy between these various measured values remains unresolved.

4.2 Extrapolation to Plasma Conditions

In order to estimate hydrogen retention and isotopic exchange in a tokamak environment it is necessary to include the effects of the distributions of energies and angles of incidence

for the hydrogen. Our model for saturation and isotopic exchange can easily include these effects by including the hydrogen depth profile for the desired energy and angular distributions.

If we assume that a surface in a tokamak will be exposed to incident hydrogen with an isotropic angular dependence and Maxwellian energy distribution, the retention and exchange behavior can be calculated. Figure 5 shows the fluence dependence of the deuterium retention expected under these conditions for TiC for a range of Maxwellian temperatures. In Fig. 6 the areal density of D retained after an incident fluence at 10^{20} atoms/cm² is plotted as a function of the characteristic particle temperature for TiC and TiB₂. The right-hand scale gives the equivalent activity in Ci/m² if the retained atoms were all tritium which allows one to estimate an upper limit for the tritium inventory in these materials. For example, if one assumes a plasma edge temperature of 1 keV for TFTR then after an incident fluence of 10^{20} T/cm² a 10% coverage of the internal surface of TFTR by TiC could retain as much as $\sim 10^{22}$ tritium atoms or ~ 500 Ci if the retained atoms were all T. This amount of T contamination is far less than the 2300 Ci allowed in readily releasable form for TFTR.¹

Figure 7 shows the calculated isotopic exchange behavior in TiC for the case of a Maxwellian energy distribution and isotropic angular dependence. The high energy tail of the Maxwellian distribution leads to a sustained gradual buildup of retained H (or T) to greater depths, and recovery of this deep component by isotopic exchange will require high fluences, i.e., long times. Thus

increasing the exposure time beyond initial saturation correspondingly increases the exchange time which will be required for a given reduction in T inventory. Other calculations show that, for the conditions given in Fig. 8, two orders of magnitude less D is required to reduce the T level to $\sim 10^{14}/\text{cm}^2$ when the D temperature is doubled (i.e., $kT = 400$ eV). This means that techniques which reduce the plasma edge temperature, such as gas puffing, should not be used during T replacement discharges.

5. CONCLUSION

In summary, our results show that hydrogen retention behavior is similar for the materials TiC, TiB₂, VB₂, B₄C, B, Si, and graphite, although the saturation concentrations differ. The amount of hydrogen retained depends on the implant depth (hence on the energy of the incident hydrogen) and on the saturation concentration for the material which can be determined from independent measurements. The saturation concentrations for these materials (at room temperature) were found to be in the range 0.16 to 0.57 hydrogen/host atom ratio. The areal density of hydrogen retained after saturation with a given incident energy was lower in TiC, TiB₂, and VB₂ by about a factor of 3 than in B, B₄C, and graphite. Our results show that none of these materials pose a serious T buildup threat if used in TFTR. We have also found that in these materials hydrogen isotopes can be replaced by subsequent implantation with a different isotopic specie so that recovery of tritium from these materials by replacement with hydrogen or deuterium should be feasible. The model we have developed to describe this process agrees very well with the data and provides predictions of retention and exchange behavior in a tokamak environment. This result is important not only from the tritium inventory standpoint but also for including wall effects in computing D-T ratios in the plasma.

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TABLE I

Material	1.5 keV Deuterium			Saturation Concentration	
	Range (Å)	Straggling (Å)	Saturation (10^{17} D/cm ²)	(10^{22} D/cm ³)	H/Host (%)
C	247	101	2.50	6.0	53
Si	335	161	1.91	2.5	50
B	216	95	3.40	5.9	45
B ₄ C	288	117	3.57	6.9	57
TiC	183	91	1.22	2.5	26
VB ₂	189	92	0.96	1.9	16
TiB ₂	208	102	1.00	1.8	16
316 SS*	100	117	3.00	8.5	100

* -120 °C

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Figure Captions

1. Calculated D concentration versus depth profiles for 1) 1.5 keV D implanted to saturation and 2) subsequent replacement with 1.5 keV H.
2. D saturation curves for the materials in this study.
3. D saturation and isotope exchange curves for 316 stainless steel at several incident energies. See text for details.
4. D saturation and isotopic replacement curves for 3 keV D_2^+ and H_2^+ on pyrolytic graphite (top) and TiC (bottom).
5. Saturation curves for a D plasma in contact with TiC at various plasma temperatures.
6. Calculated D retention as a function of plasma temperature for TiC and TiB_2 samples exposed to fluences of 10^{20} D/cm².
7. Calculated saturation and isotopic replacement curves for T in TiC. Both the T and the replacing ion, D, have temperatures of 200 eV. The 3 curves A, B, and C show the replacement of T by D after T fluences of 10^{18} , 10^{19} , and 10^{20} /cm², respectively. Notice that an order of magnitude more D than T must be implanted to bring the retained T down to 10^{15} /cm².













