CTR and Related Phenomena
HYDROGEN IN FUSION FIRST WALL SURFACES*
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Summary

The concentration at which deuterium implanted into the materials B, C, Si, TiC, TiB2, B4C, and VB2 saturates has been measured using nuclear microanalysis. The local mixing model for H saturation and isotopic replacement agree well with these data and yield H saturation concentrations close to 0.5 H/host atom ratio for the elemental samples and lower concentrations for the compounds. The local mixing model has also been used to model tritium buildup and isotope exchange in proposed first-wall materials for magnetic confinement fusion reactors. Two statistical models are introduced to discuss the buildup to saturation.

Introduction

The accumulation of ion-implanted hydrogen (H, D, T) in the near surface region of solids has recently received much study. This interest has been generated largely by the ramifications of this accumulation in components such as limiters or other first-wall surfaces of magnetic confinement fusion reactors (e.g., tokamaks and mirrors). In particular, the near-surface build-up of H-isotopes strongly affects the recycling process (1) and may lead to unacceptable levels of T.

H saturation is also of interest from a basic physics viewpoint. Unfortunately the ion-implantation process complicates the normal solid state considerations such as diffusion, crystallinity, solubility, etc., through effects such as damage production, trapping, nonequilibrium thermodynamics, swelling, and blistering. Although in a few cases H saturation has been correlated to swelling and blistering of the surface (2), current explanations (3-6) of this behavior are primarily phenomenological.

In the present work data for the near surface H accumulation are presented for several low atomic number materials and are compared to predictions of the Local Mixing Model (LMM) of H saturation and isotope exchange. The LMM has also been used to predict tritium buildup and recovery characteristics when these materials are exposed to fusion plasma conditions (i.e., incident ions with Maxwellian velocity distributions). In the final sections of the paper the buildup to saturation is examined, and two statistical descriptions are presented.

Experimental

The samples studied in this investigation were the elements B, C, and Si, and compounds TiC, B4C, TiB2, and VB2. All of these materials (except Si) have high melting temperatures and low atomic numbers of interest for fusion applications. The B was formed by chemical vapor deposition (CVD) on a graphite substrate, the C was in the form of pyrolytic graphite and Papyex and the silicon was single crystal. Both the TiC and TiB2 were formed by CVD. The VB2 was made by boriding vanadium and the B4C was hot pressed.

The hydrogen retention and replacement properties of these materials were studied by implanting H or D at an energy of 1.5 keV/amu using a Colutron ion accelerator. At these energies little or no blistering is anticipated (7). All implants were carried out at ambient temperatures and the fluence uniformity was measured to be ±10%. Because of the low power deposited in the targets during both implant and analysis, the target temperature should not have exceeded 50°C.

The total amount of H or D retained within 500 nm of the surface was monitored as a function of incident fluence using D(3He,p) nuclear reaction analysis (NRA) for D with 3 MeV He ions. H(19F,α) resonant nuclear reaction analysis (RRA) profiling was used to detect H using 6.4 MeV 19F. Elastic Recoil Detection (ERD) was used in some cases to simultaneously measure the total amounts of H and D (8,9). An example of an ERD measurement of H plus H implanted C is shown in Fig. 1.

Figure 1. D and H retention as a function of incident fluence. These measurements were performed using the ERD technique and the panels above the figure show raw spectra. The lines are predictions of the LMM theory.

In all of the materials examined, and in particular the C in Fig. 1, it was found that, at low fluences (<5x1018 cm-2) all the incident H (or D) was retained in the sample, apart from the small fraction (typically 5-10%) kinematically reflected. As the incident fluence was increased, a maximum hydrogen concentration (saturation) was eventually reached in each of these materials. To further characterize this H build up and to simulate gas changeover in a fusion reactor, we implanted the D saturated samples with H and monitored the D and H content as the H displaced the D. Retention for this case is shown on the right side of Fig. 1 where the sharp break in the D retention curve marks the shift to H.
implantation. The solid and dashed lines show results predicted by the local mixing model (10,11) which is described in the next section. All of the materials examined showed similar saturation and isotopic exchange behavior.

![Graphs showing D and H retention in carbon as a function of fluence for various overlap conditions of the D and H depth profiles. The implant conditions are given in each panel.](image)

**Figure 2.** D and H retention in carbon as a function of fluence for various overlap conditions of the D and H depth profiles. The implant conditions are given in each panel.

**Discussion**

The Local Mixing Model

The local mixing model is a phenomenological model used to describe H saturation and isotope exchange behavior which treats the exchange differentially in depth. A detailed explanation of this model is given in references (10) and (11). This model assumes that for every H or D (or T) atom which comes to rest in a region on the material that is saturated one H atom is lost so that the local (H/D)/host atom ratio never exceeds the saturation concentration. The probability that the displaced atom is H or D is given by the ratio of the local H or D concentrations to the saturation concentration, respectively. Incident H or D atoms stopping in regions where the concentration is below saturation are retained. The model uses theoretically (12) calculated D and H deposition profiles, and the saturation concentrations for the various materials are determined from retention measurements. The saturation D concentrations \( n_{\text{sat}} \) which provide the best fits to the data are listed in Table 1. These concentrations can also be directly measured using high resolution profiling techniques. No additional free parameters are required to describe the saturation-exchange with this model.

<table>
<thead>
<tr>
<th>Material</th>
<th>B/C</th>
<th>Si</th>
<th>TiC</th>
<th>TiB2</th>
<th>VB2</th>
</tr>
</thead>
<tbody>
<tr>
<td>( n_{\text{sat}} )</td>
<td>0.45</td>
<td>0.40</td>
<td>0.50</td>
<td>0.57</td>
<td>0.26</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.16</td>
</tr>
</tbody>
</table>

To verify the predictions of the LMM as a function of incident particle energy, isotope exchange measurements were made in graphite using different incident energies for H and D to change the overlap between the depth profiles of the two isotopes to alter the exchange behavior. When the H and D are both implanted at 1.5 keV (Fig. 2a), the H and D profiles overlap very closely. The model shows that, for this case, D on the deep side of the profile is difficult to replace because fewer H atoms stop at this depth than at the peak. Decreasing the H energy to 1 keV (Fig. 2b) shifts the H profile toward the surface such that more of the D on the deep side of the profile remains in the sample. Decreasing the initially implanted D energy to 1 keV (Fig. 2c) shifts the D profile toward the surface such that deeper D is more easily replaced by H. The good agreement between the data (dots) and the model (lines) indicates that the LMM contains the correct dependence on the incident particle energy. Underwood, et al (13) have also observed a decrease in the D replacement rate for non-overlapping profiles by measuring the release of D2 and HD gas from D saturated carbon during H implantation.

Another prediction of the LMM is that the onset of isotope exchange occurs when saturation is reached. This prediction has been tested by first implanting graphite with a low fluence of D and then continuing the implantation with H to a high fluence. The result of this experiment is shown in Fig. 3. Indeed, the retained D does not decrease until saturation is attained. A similar effect has been observed recently by Schultz, et al (14) for the replacement of D by \(^{3}\)He in Mo at low temperature.

![Graph showing D retention versus H fluence for an unsaturated carbon sample.](image)

**Figure 3.** D retention versus H fluence for an unsaturated carbon sample.
The excellent agreement between the LMM and the data shown in Figs. 1-3 supports the validity of the basic assumption of the model that the essential physics of the saturation and exchange process occurs at the end of the H trajectory.

Fusion Plasma Conditions

The hydrogen ions incident on materials in a fusion reactor are generally not monoenergetic but have a distribution of energies. To model this situation, the retention and exchange of tritium by deuterium with a Maxwellian velocity distribution in TiC has been calculated using the LMM. Results of these calculations are summarized in Fig. 4. The initial tritium plasma for these calculations had $kT = 200$ eV. The plasma is changed from T to D of the same energy when the T fluence to the walls reach levels of $10^{18}$, $10^{19}$, and $10^{20}$/cm². These change-overs are labeled A, B, and C, respectively in the figure. The high energy tail of the Maxwellian distribution leads to a sustained gradual build up of retained T at greater depths, and recovery of this deep component by isotopic exchange will require high fluences. In other words, T recovery from the walls of a fusion reactor, coated with a material like TiC, through isotopic replacement with D, is feasible but would require considerable time; however, smaller amounts of T replacement, say 1/2, could be accomplished with only a few D discharges.

Other calculations presented in Fig. 5 show that, for the conditions given in Fig. 4, considerably less D is required to reduce the T level when the D plasma temperature is doubled (i.e., $kT = 400$ eV). Thus techniques which reduce the plasma edge temperature such as gas puffing should not be used during T replacement discharges. Glow Discharge Cleaning (GDC) could also be used for isotope exchange. One application of GDC might be to preload surfaces of first-walls with H isotopes in order to control recycling. For example, in an igniting fusion reactor, the optimum wall loading of D and T would have - 50% T and D. This loading could be achieved by GDC even before the first plasma is struck.

Figure 4. Calculated saturation and isotopic replacement curves for tritium in TiC. The local mixing model was used assuming a Maxwellian velocity distribution. The curves labeled A, B, and C indicate changes to D plasmas when the T fluence reaches $10^{18}$, $10^{19}$, and $10^{20}$/cm², respectively.

Figure 5. LMM calculations of T retention and replacement by 200 eV D (dashed line) and 400 eV D (solid line).

Approach to Saturation

Two macroscopic models which have been used to describe the build up to saturation of retained D or H are 1) an exponential approach of the local concentration to a maximum level $n_{sat}$ or 2) a truncation (4) of the depth profile for concentrations greater than $n_{sat}$. In the exponential approach, the probability that a D atom is not retained in the material is assumed to be equal to the fraction of D already present at that depth relative to the saturation concentration

$$n_{e}(x) = n_{sat}(1 - \exp(-\Phi(x)/n_{sat})),$$

where $n_{e}(x)$ is the D concentration at depth x calculated using the exponential approach model, $\Phi(x)$ is the incident fluence and $P(x)$ is the probability density that the D comes to rest at x. For the truncation picture the retention probability is unity until saturation is reached and zero after saturation, i.e.,

$$n_{x}(x) = \text{MIN}(\Phi(x)/n_{sat})$$

where the t subscript indicates truncation. The total amount of D retained is calculated by evaluating the integral

$$N_{D} = \int_{0}^{\infty} n(x)dx.$$

The predictions of these two models for 1.5 keV D on C are plotted in Fig. 6. The truncation picture clearly provides the best fit to these data, which indicates that the trapping probability, at least on a macroscopic scale, must be extremely high.

What does this high retention probability imply on an atomistic scale? Consider the final major collision in a D ion's traversal of a solid. For the purposes of illustration, imagine that, during this end-of-range encounter, three D trap sites are activated. The exact identity of these traps has yet to be ascertained, but the general consensus is that they involve damage induced by the implant beam. If one of the activated traps already contains a D atom, we assume that this atom becomes temporarily detrapped. Therefore, the intermediate state of this system consists of two D atoms...
atoms competing for three vacant traps. At this stage two viewpoints can be considered, which we label 1) short range and 2) long range trapping.

For the case of short range trapping it is assumed that as the local excited region "cools" each D or H atom will become localized near a trap site. This scenario is shown graphically in Fig. 7a. In this figure, the trap (squares) with no D near it quickly deactivates and therefore plays no role in determining the retention probability for this particular system. The three final states of this system (i.e., no D, 1 D or 2 D's trapped) is easily calculated using binomial statistics.

The comparable long range trapping case is illustrated in Fig. 7b. In this situation each D can eventually end up in any of the three sites. The mathematical description of the long range trapping is much more complicated than that of short range trapping and requires a more sophisticated statistical solution. Details of both statistical models will be given elsewhere (15).

Three variables are common to both pictures: 1) p, the probability for trapping one D by one vacant site, 2) s, the number of trapping sites assumed to be in each end-of-range trap cluster (s = 3 in the example diagrammed in Fig. 7) and 3) r, the number of trap sites per host atom. The local concentrations of D at a depth x is calculated using both pictures are obtained by using the calculated depth profile of D to determine the number of D ions which end their trajectories at x and by noting that the number of D visits a specific cluster of s traps obeys Poisson statistics.

Predictions of these two trapping models for 1.5 keV D on C are plotted along with the results of the exponential and truncation approaches in Fig. 6. The parameters used for these curves were p = .94, s = 15 and r = .5 for the short range model and p = .88, s = 4 and r = .5 for the long range model. These values for s were the maximum allowable for the long range model because of computational restrictions. Better fits to the data would have been obtained if higher values of s were used. For p = 1 and s => the two statistical theories reduce to the truncation model. This implies, as anticipated by the success of the truncation model, that a large number of sites are involved in the trapping of each D atom and that the trapping probability for one trap to catch one D must approach unity. The fact that a large number of trapping sites must be activated by each D collision is consistent with the view that the D is trapped in microscopic open volumes either preexistent or induced by charged radiation. A related conclusion has been given by Botston (3) for D trapping in stainless steel at low temperature.

**Conclusion**

Our results show that hydrogen retention and isotopic exchange behavior is similar for the materials B, C, Si, TiC, B4C, TiB2, and VB2, although the saturation concentrations differ. Although local T concentrations may become high, none of these materials should pose a serious T buildup threat if used in a fusion reactor because the T atoms will be restricted to the very near surface region. We have also found that in these materials hydrogen isotopes can be replaced by subsequent implantation with a different isotopic specie so that tritium recovery by replacement with hydrogen or deuterium is feasible.

**References**

8. An excellent review of all of these H measurement techniques is given by J. F. Ziegler, Appl. Phys. Lett. 31, 544 (1977).

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**Figure 6.** Saturation curves for 1.5 keV D on carbon. The points are experimental and the four curves correspond to calculations using the exponential approach, truncation approach, and the two statistical models described in the text.

**Figure 7.** Diagram of the end-of-range H trapping for a) short range trapping and b) long range trapping. The squares indicate activated traps and the H symbol represent hydrogen or deuterium atoms.