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# Effects of lithium-implantation on the hydrogen retention in both a-C:H and a-SiC:H materials submitted to deuterium bombardment

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## Abstract

The hydrogen release in plasma facing materials is a challenging problem for the hydrogen recycling. The hydrogen desorption from the a-C:H and a-SiC:H materials induced by deuterium bombardment has been investigated. Prior to the deuterium bombardment, both materials were implanted with different fluences of lithium ions. Before and after each irradiation, depth profiles of H, Li and deuterium were determined by nuclear microanalysis. After deuterium bombardment, it is shown that the retention of the initial hydrogen in both materials was enhanced by increasing the total dose of the implanted Li. For the a-C:H samples, the hydrogen desorption under deuterium bombardment was strongly reduced by lithium implantation. This effect was also evidenced in a-SiC:H samples, even though it is less spectacular than in a-C:H. Also, nuclear analyses showed that the retained dose of deuterium decreases when the lithium concentration increases. This could be a result of the formation of Li–H bonds which occurs to the detriment of deuterium retention in both a-C:H and a-SiC:H materials. Preliminary results of both materials exposed to TdeV tokamak discharges confirms the role of Li in hydrogen retention, already observed in deuterium bombardment exposure.

*Keywords:* Tolev; Tokamak; Desorption; Low *Z* wall material

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## 1. Introduction

Production of energy by means of fusion reactors requires control of the hydrogen recycling. Hydrogen release and retention considerably affects the control of the plasma density during tokamak discharges. Lithium has recently shown very interesting results in the control of impurity production and hydrogen recycling between the plasma and the facing materials [1–4]. Snipes et al. [1] have shown that the injection of Li pellets into TFTR discharges improved significantly the wall conditioning by lowering the C sputtering yield of the limiters. Terreault et al. [2] have confirmed that the injection of small quantities of lithium in the plasma during the discharges of TdeV (Tokamak de Varennes) caused an increase in the wall pumping capacity of impurities, as a result of not only a reduction of carbon erosion (due to O-gettering) but also an appreciable reduction in D-recycling. A hydrogen retention due to the formation of Li–H bonds was also observed when lithium thin films were submitted to H discharges [3].

Amorphous hydrogenated carbon (a-C:H) has been widely studied for plasma facing materials applications [4–8]. However, in addition to its relative weak hydrogen retention [6], this material was found to be easily eroded [5–7]. Amorphous hydrogenate silicon carbide (a-SiC:H) appears as a promising material to be used in the tokamak environment due to its thermal and chemical stabilities. In this paper, we will compare the H retention in both a-C:H and a-SiC:H films under deuterium bombardment. The effect of lithium implantation in these materials will be investigated. Preliminary results of both a-C:H and a-SiC:H materials exposed to the plasma in the scrape-off layer of TdeV (tokamak de Varennes) will be also presented.

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## 2. Experimental

The a-C:H and a-SiC:H films were prepared at INRS-Énergie et Matériaux using a plasma enhanced chemical vapor deposition (PECVD) reactor. They were deposited on silicon wafers. More details were reported elsewhere [9]. $^7$Li was implanted at the IPNL (Institut de Physique Nucléaire de Lyon) normal to the surface with an energy of 8 keV, a beam current limited to $\sim 4$ $\mu$A/cm$^2$ and at different fluences ($2$–$20 \times 10^{16}$ Li/cm$^2$).

Deuterium irradiations were performed by means of an ion implanter at INRS, under normal incidence with a density current of about 0.1 mA/cm$^2$. A few as-deposited a-SiC:H and a-C:H samples were first implanted at 1.2 keV with various fluences (1.5 to $7.5 \times 10^{16}$ D/cm$^2$) in order to measure the accurate mean range. As-deposited and Li-implanted samples were then irradiated with following energies and fluences (1.2 keV, $3.5 \times 10^{16}$ D/cm$^2$ and 3.3 keV, $6.75 \times 10^{16}$ D/cm$^2$) in order to form a flat concentration profile over the first hundred nanometers. Some as-deposited and Li-implanted samples of a-C:H and a-SiC:H were also exposed in the scrape-off layer of TdeV. Samples were submitted to 20 discharges ($n_e = 2.5 \times 10^{19}$ m$^{-3}$, $I_p = 170$ kA, $B_t = 1.4$ T, $T_e = 800$ eV), followed by 4 plasma-disruptions. The discharge lasts $\sim 1.2$ s. More information on the TdeV geometry and parameters can be found in Ref. [8].

The film thicknesses (0.45 $\mu$m for a-C:H, and 1.8 $\mu$m for a-SiC:H) were measured by cross-section observations under a scanning electron microscope. X-ray photoelectron spectroscopy (XPS), NRA (nuclear reaction analysis), RBS (Rutherford backscattering spectrometry) and ERD $E \times B$ (elastic recoil detection coupled with an electromagnetic field) [10,11] were also used to characterize the layers. The composition of the as-deposited films was a-Si$_{0.4}$C$_{0.3}$:H$_{0.3}$ and a-C$_{0.65}$H$_{0.35}$. Their densities were 2.35 g/cm$^3$ and 1.9 g/cm$^3$ for a-SiC:H and a-C:H, respectively. The areal density of retained Li was determined using the $^7$Li(p, $\alpha$)$^4$He reaction at 2.5 MeV. These analyses were performed at the 4 MV IPNL Van de Graaff. Deuterium was characterized by means of the ERD $E \times B$ technique using 2.8 MeV $^{20}$Ne and 2.6 MeV $^{15}$N beams. The ion beam is incident at an angle of 15° with respect to the surface of the sample. The D$^+$ recoils are energy-analyzed at an angle of 30° to the beam in a low noise ion-implanted silicon detector. The intensity of the incident beam was limited to $\sim 20$ $\mu$Cb, therefore the technique had a sensitivity of $\sim 1$ at% and a depth resolution (standard deviation) of 4 nm at the surface. As the energy of the recoil-deuterium was $\sim 700$ keV, charge fractions of D$^0$ and D$^-$ were negligible. The spectra were deconvoluted into depth profiles with the program Alegria [12] which uses TRIM95 [13] measured stopping powers for ions in a-SiC:H and a-C:H. The depth profiles of deuterium close to the surface were also analyzed at INRS with a 350 keV $^4$He beam. After each step of implantation and irradiation, hydrogen depth profiles were also measured with the IPNL ERD $E \times B$ facility using a 2.5 MeV $^4$He beam. ERD cross sections were given in [14]. XPS and SIMS (secondary ion mass spectroscopy) techniques were also used to determine the change in the very-near surface of the sample exposed in TdeV.

## 3. Results and discussion

### 3.1. a-C:H samples

Fig. 1 shows the evolution of the hydrogen profiles after each step of implantation and irradiation. The corresponding depth profiles of Li and D are shown. Samples of a-C:H samples were implanted with two doses of Li (4 and $10 \times 10^{16}$ Li/cm$^2$). Depth profiles of an as-deposited a-C:H sample submitted to the same deuterium irradiation are also shown.

In a-C:H, even at a fluence of $2 \times 10^{17}$ at/cm$^2$, lithium saturation is not yet reached. However, as shown in Table 1, mean ranges and variances drastically increase with the implanted dose. For low fluences ($\leq 4 \times 10^{16}$ Li/cm$^2$) mean ranges of implanted Li are in agreement with TRIM95 [13] calculations. However, experimental variances are found to be more than twice larger than TRIM. This may be a consequence of the high diffusivity of lithium atoms in a-C:H films.

After lithium implantation, a low contamination of both carbon and oxygen was observed in the very near surface

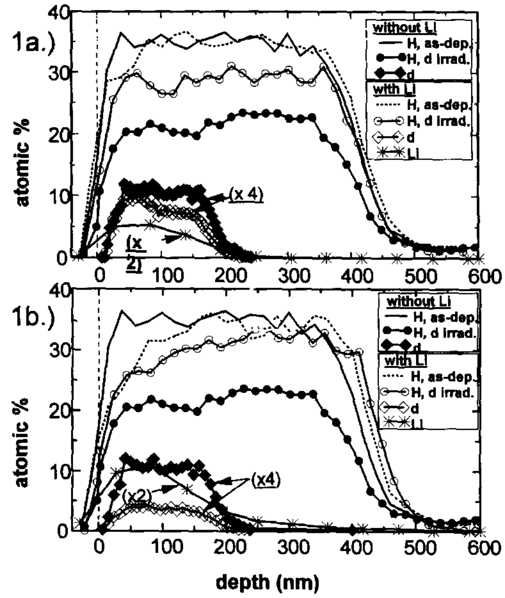

Fig. 1. Depth profiles of H, Li and D in as-deposited (without Li) and Li implanted $4 \times 10^{16}$ (Fig. a with Li) and $1 \times 10^{17}$ Li/cm$^2$ (Fig. b with Li) a-C:H samples.

by means of RBS. Particularly the oxygen contamination ($0.5 \times 10^{16}$ O/cm$^2$ for an implanted dose of $1 \times 10^{16}$ Li/cm$^2$) showed a diffusion-like profile which covers the Li-stopping zone. This surface contamination could explain the in-depth-shift of the H profiles before and after lithium implantation (Fig. 1). The total amount of hydrogen within the a-C:H film was measured and included in Table 2. It remained nearly constant before and after lithium implantation. So, the decrease of hydrogen concentration in the first ten nanometers is likely due to in-depth hydrogen migration.

The measured mean range of the implanted deuterium profile at 1.2 keV in as-deposited a-C:H samples is much larger than the TRIM calculations (Table 1). However, the mean range of deuterium implanted under similar conditions at 1.2 keV in a Si sample was found to be very close to TRIM. Such a difference for our samples cannot be attributed to the analysis technique (performed with 3 different ion beams at two different laboratories). This could be a consequence of initial hydrogen and its effect (not taken in account in TRIM calculations) on deuterium transport in a-C:H films.

The hydrogen concentration in an as-deposited a-C:H sample exposed to $1.2 \times 10^{17}$ D$^+$/cm$^2$ (at 1.2 and 3.3 keV) was strongly reduced (about $6 \times 10^{17}$ atoms/cm$^2$) (Table 2 and Fig. 1). A large quantity (40%) of the initial hydrogen was removed over the four hundred nanometers, whereas deuterium penetrates only to a depth of about 200 nm. This surprising effect was probably not induced by thermal desorption during bombardment (although no temperature measurement has been done yet), because only a low power (~ 1 W) was deposited on the surface during implantation. More likely, a large quantity of the initial hydrogen, which was weakly bonded, could diffuse and be desorbed. In the Li-implanted samples submitted to the same fluences of deuterium, the H desorption was strongly reduced. (Fig. 1 and Table 2); 20% and 10% of the initial hydrogen was removed when $4 \times 10^{16}$ and $1 \times 10^{17}$ Li/cm$^2$ were previously implanted in a-C:H samples, respectively. This striking effect could be partially explained by the formation of Li–H bonds. However, by comparing the retained dose of H after deuterium bombardment for both Li-implanted and as-deposited a-C:H films, we found that an implantation of $1 \times 10^{17}$ Li/cm$^2$ results in a retention of $6 \times 10^{17}$ H/cm$^2$. This suggests that Li-implantation enhances the H-retention of a-C:H films by not only forming Li–H bonds but also by stabilizing the initial C–H bonds.

Table 1
Comparison of the measured mean range of lithium and deuterium implanted in a-C:H and a-SiC:H at different doses

| | a-C:H | | a-SiC:H | |
|---|---|---|---|---|
| | $R$(nm) | $\Delta R$(nm) | $R$(nm) | $\Delta R$(nm) |
| *Li, 8 keV* | | | | |
| $2 \times 10^{16}$ cm$^{-2}$ | 80 | 70 | | |
| $4 \times 10^{16}$ cm$^{-2}$ | 94 | 60 | 68 | 65 |
| $1 \times 10^{17}$ cm$^{-2}$ | 111 | 85 | 79 | 57 |
| $2 \times 10^{17}$ cm$^{-2}$ | 133 | 88 | | |
| TRIM95 | 85 | 30 | 59 | 29 |
| *D, 1.2 keV* | | | | |
| $1\text{–}7 \times 10^{16}$ cm$^{-2}$ | 44 | 20 | 39 | 16 |
| TRIM95 | 32 | 11 | 26 | 12 |

Table 2
Total amount of hydrogen (from 0 to 500 nm in a-C:H, from 0 to 125 nm in aSiC:H) and deuterium in as-deposited and Li-implanted samples submitted to deuterium irradiation

| | Hydrogen | | Deuterium |
|---|---|---|---|
| | before D irrad. | after D irrad. | |
| *a-C:H* | | | |
| $4 \times 10^{16}$ Li cm$^{-2}$ | $1.35 \times 10^{18}$ | $1.10 \times 10^{18}$ | $2.9 \times 10^{16}$ |
| $1 \times 10^{17}$ Li cm$^{-2}$ | $1.37 \times 10^{18}$ | $1.25 \times 10^{18}$ | $1.3 \times 10^{16}$ |
| without Li | $1.34 \times 10^{18}$ | $7.51 \times 10^{17}$ | $3.9 \times 10^{16}$ |
| *a-SiC:H* | | | |
| $4 \times 10^{16}$ Li cm$^{-2}$ | $4.32 \times 10^{17}$ | $4.22 \times 10^{17}$ | $8.7 \times 10^{16}$ |
| $1 \times 10^{17}$ Li cm$^{-2}$ | $3.82 \times 10^{17}$ | $3.80 \times 10^{17}$ | $8.2 \times 10^{16}$ |
| without Li | $4.37 \times 10^{17}$ | $3.75 \times 10^{17}$ | $1.1 \times 10^{17}$ |

The deuterium retention was surprisingly very low (Table 2 and Fig. 1) in the as-deposited samples. only ~ 25% of incident deuterium ions remained in the sample (about 100% of deuterium in as-deposited a-SiC:H was retained, as it will be seen later). This shows that not only hydrogen but also deuterium was strongly released under the effects of deuterium bombardment. In Li-implanted samples, the retention was more reduced (9% instead of 25%). This result suggests that the larger quantity of hydrogen retained by the Li-implantation would occupy all the hydrogen (deuterium) traps and would modify the recycling of impinging hydrogen (deuterium).

### 3.2. a-SIC:H samples

The H, Li, and D depth profiles for both as-deposited and Li-implanted a-SiC:H-samples are shown in Fig. 2a and b for $4 \times 10^{16}$ and $1 \times 10^{17}$ Li/cm$^2$ implanted fluences, respectively. The profiles were measured before and after deuterium irradiation. As observed in the a-C:H samples, C and O contamination found after Li implantation could be responsible for the in depth-shift of the hydrogen profile (Fig. 2). The range of Li implanted in a-SiC:H was found to increase with the Li fluences. However, hydrogen diffusion is less important than in a-C:H (total amount of H was found to be constant; see Table 2). It is worth noting that the range of deuterium ions implanted at 1.2 keV in aSiC:H (Table 1) is much larger in our experiments than in TRIM calculation (as observed for

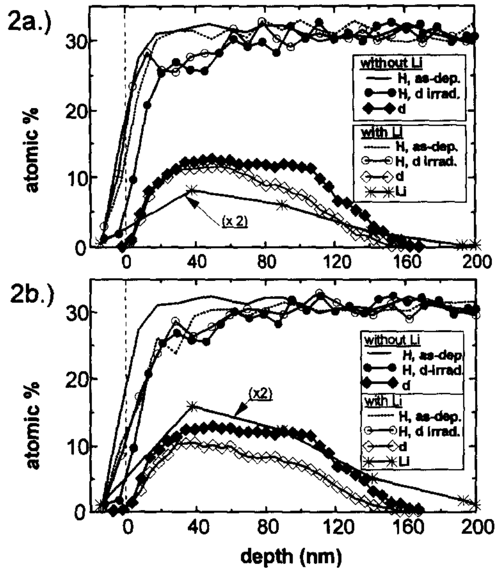

Fig. 2. Depth profiles of H, Li and d in as-deposited (without Li) and Li implanted $4 \times 10^{16}$ (Fig. a with Li) and $1 \times 10^{17}$ Li/cm$^2$ (Fig. b with Li) a-SiC:H samples.

a-C:H), although experimentally measured ranges (in our laboratory) of deuterium implanted at 1.25 keV in SiC were found to compare well with TRIM predictions [15]. This suggests that the difference between our experiments and TRIM is due to the presence of the hydrogen in our a-SiC:H films.

The effect of deuterium bombardment on hydrogen profiles was found to be less prominent in a-SiC:H films than in a-C:H films. The total amount of desorbed H in an as-deposited a-SiC:H sample exposed to $1.2 \times 10^{17}$ D/cm$^2$ (at 1.2 and 3.3 keV) is about $6 \times 10^{16}$ as compared to $6 \times 10^{17}$ in the a-C:H (Table 2 and Fig. 2). The hydrogen seems to desorb only from the first hundred nanometers in the a-SiC:H samples. The effect of Li-implantation is less pronounced than in a-C:H films, because the hydrogen is more strongly bonded in a-SiC:H than in a-C:H films. Note that the retention of implanted deuterium was lower in Li-implanted samples (Fig. 2 and Table 2).

### *3.3. Samples exposed in the scrape off layer of the TdeV tokamak*

As-deposited and Li-implanted a-C:H samples were exposed in the scrape-off layer of TdeV perpendicular to the magnetic field lines and facing the electron-drift direction at a distance of about 44 mm from the separatrix. RBS measurements indicated that for both samples a thin layer (about 50 nm) was sputtered away, while XPS analysis showed the presence of a low amount of contaminants (Fe, O, C, B) at the surfaces. It is thought that surface erosion occurred during the first 16 discharges, while contamination more likely resulted from the last four disruptions. Fig. 3 shows the H depth profiles in both as-deposited and $2 \times 10^{17}$/cm$^2$ Li-implanted samples before and after TdeV expositions. Depth profiles of deuterium, which was incorporated during the TdeV discharges, are also reported in the inset of Fig. 3. It is clearly observed that H was strongly released (in both as-deposited and Li-implanted samples) over a depth that widely exceeds the depth in which deuterium was incorporated. This suggests that the heating of the sample by the plasma may enhance the detrapping and the diffusivity of H in a-C:H. The release of hydrogen was clearly reduced in the Li-implanted samples. This could be interpreted by the enhanced H-retention in the films as a consequence of Li–H bonds formation. Moreover, the Li-implanted layer also limits hydrogen release by acting as a diffusion barrier. At the same time, the incorporated amount of deuterium was lowered in Li-implanted sample, as compared to the as-deposited a-C:H sample. This confirms the observed results on the deuterium bombardment (Table 2). It seems that the initial hydrogen in Li-implanted samples is more stable (due to chemical bonds or diffusion barrier), then the bombarded deuterium would be in excess in the sample and would not be trapped. So, the implantation of lithium in the sample would have promising benefits on the hydrogen recycling.

Few a-SiC:H (as-deposited and Li-implanted samples) were exposed in TdeV parallel to the magnetic field lines and facing the plasma. In both cases, a composed contamination layer (C, B, Fe, O) was observed at the sample surface. Because of this impurity deposition we cannot conclude on the role of implanted Li. However, it is worth mentioning that only a little quantity of hydrogen was released from the a-SiC:H samples.

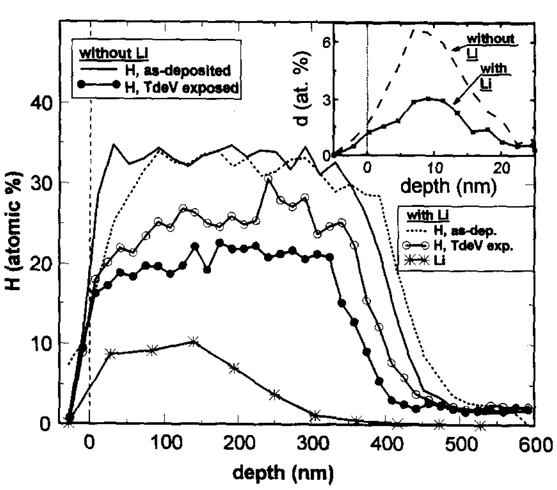

Fig. 3. Depth profiles of H, Li and d in as-deposited (without Li) and Li implanted $2 \times 10^{17}$ Li/cm$^2$ (with Li) a-C:H samples.

## 4. Conclusion

The hydrogen desorption in as-deposited a-C:H layers submitted to irradiation (deuterium or TdeV plasma fluxes) is very large and widely overtakes the irradiated zone. This suggests that the bombarding particles (implanted deuterium and plasma ions) may enhance the detrapping and the diffusivity of H in a-C:H. The implantation of Li near the surface prior to the irradiation strongly reduces the hydrogen release from 40% to 20% (with $4 \times 10^{16}$ Li/cm$^2$) and to 10% ($1 \times 10^{17}$ Li/cm$^2$). In addition, the Li implantation was found to reduce the deuterium retention (coming from the ion beam or the TdeV plasma). This improved behavior of Li-implanted a-C:H films is probably due to the formation of Li–H bonds, which prevent the H desorption and diffusivity.

The retention of H in as-deposited a-SiC:H samples is already stronger than in Li-implanted a-C:H samples. So, the effects of Li-implantation on the hydrogen retention are less prominent than in a-C:H films, although slight differences were observed. Finally, this work shows that in addition to its previously demonstrated benefits on oxygen gettering, the implantation of Li in plasma-facing materials can help to control the hydrogen recycling.

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