Trapping and thermal diffusion for energetic deuterium implanted into SiC

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A R T I C L E    I N F O

Article history:
Received 13 November 2015
Revised 10 February 2016
Accepted 17 March 2016
Available online xxx

Keywords:
SiC
Deuterium implantation
Thermally stimulated desorption
Diffusion
SIMS

A B S T R A C T

During ITER and DEMO reactor operation Li–Pb blanket flow channel inserts made from SiC will be exposed to both radiation and tritium. Absorption, desorption, and tritium diffusion are expected to occur and will strongly depend on the irradiation conditions; temperature, and neutron and gamma fluxes. Reaction bonded (RB) SiC samples were deuterium implanted at both room temperature and 450 °C at different implantation energies and the corresponding TSD spectrum was obtained for each implantation energy. After implantation the samples were subjected to SIMS analysis. The TSD spectra obtained for all the samples implanted at different energies are very similar and characterized by a prominent deuterium desorption occurring at temperatures between 450 and 1000 °C with a maximum that exhibits a clear trend to shift toward higher temperature as either implantation energy or implantation temperature increase. SIMS analysis before heating the deuterium implanted samples indicates that the implanted deuterium has a tendency to become bonded to Si rather than to C. The SIMS analysis shows that once heated up to 1000 °C only part of the implanted deuterium was thermally released. The temperature shift observed when increasing the deuterium implantation energy and, hence, penetration, implies a deuterium diffusivity value at 700 °C of about 8.5 × 10⁻¹⁷ m²/s.

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Introduction

SiC materials are primary candidates for flow channel inserts in blankets due to their excellent thermo-mechanical and corrosion properties [1,2]. For this application hydrogen isotope absorption is of fundamental importance. During reactor operation the SiC material will be exposed to tritium in a hostile radiation environment. Absorption, diffusion, and desorption are expected to occur, depending strongly on the radiation conditions, neutron flux, and, ionizing radiation. The operation temperature for this material in a future fusion reactor could be from about 500 up to 1000 °C depending on the type of blanket concept [3]. The main aim of this work is to study the behaviour of energetic deuterium implanted into SiC in terms of trapping, detrapping, and diffusion within the temperature range of between 400 and 1000 °C.

Reaction bonded (RB) SiC samples were deuterium implanted at both room temperature and 450 °C at different implantation energies. The implantation energies used for this work ranged from 20 keV up to 50 keV. After deuterium implantation, the samples were heated up to 1000 °C at a rate of 0.16 °C/s and the deuterium released was measured as a function of temperature obtaining in this way the corresponding Thermo Stimulated Desorption (TSD) spectrum for each implantation energy. After implantation the samples were subjected to secondary ion mass spectrometry (SIMS) analysis both before and after being heated up to 1000 °C.

The TSD spectra obtained for all the samples implanted at different energies are very similar and characterized by a prominent deuterium desorption occurring at temperatures between 450 and 1000 °C with a maximum that exhibits a clear trend to shift toward higher temperature as either implantation energy or implantation temperature increase. The temperature shift observed when increasing both the deuterium implantation energy and, hence, penetration, implies a deuterium diffusivity value near 700 °C of about 8.5 × 10⁻¹⁷ m²/s within the range of the value expected from the diffusivity parameters found in the literature [4].

Experimental procedure

1 mm thick RB SiC samples (ρ = 3.10 g/cm³), were cut and optically polished from the same 15 mm diameter bar (Goodfellow) to ensure uniformity. This commercially available RB material has low apparent porosity (0%), fine grained, and highly crystalline (90%
hexagonal phase and 10% free crystalline silicon, typical impurities; B, Al, N, Fe, Mo). Further microstructural characterization is given in a previous work [5]. Before being deuterium implanted all the samples were heated up to 1000 °C in vacuum (2 × 10^{-6} mbar) for 2 h in order to clean the sample of vapours, gases, and humidity.

Two of the samples were deuterium implanted at 25 °C with 20 and 50 keV respectively with deuterium ions (D\(^+\)), at 0.5 microamp/cm\(^2\), up to a dose of 1 × 10^{16} ions/cm\(^2\), at the CEMAT Danysik 60 kV ion implanter. In order to study both the dose and the temperature effect another two samples were implanted up to a higher dose of 1 × 10^{17} ions/cm\(^2\) with 20 keV D\(^+\) at 0.5 microamp/cm\(^2\), one of them was implanted at 25 °C and the other at 450 °C.

Once deuterium implanted, each of the samples was consecutively mounted in a special cell provided with an oven which permitted to heat the samples from 25 up to 1000 °C. A helium leak detector was connected to the cell in order to measure the D\(_2\) implanted into the samples. In this way TSD measurements were carried out. The sensitivity for this TSD measuring system was equivalent to ≥ 5 × 10^{-12} (mbar l)/s or 0.13 × 10^{9} D\(_2\)/s. For all the samples the heating rate during TSD measurements was 0.16 °C/s and the background pressure was 2 × 10^{-6} mbar.

Before and after the TSD measurements, the deuterium implanted samples were analysed using SIMS (Hiden Analytical, 5 kV O, 150 nA) to compare the amount of deuterium remaining as a function of depth, determined using a profilometer to measure the final sputter crater depth. For the higher implantation dose (1 × 10^{17} ions/cm\(^2\)) deuterium was clearly detected by SIMS meanwhile for the samples implanted at the lower dose (1 × 10^{16} ions/cm\(^2\)) it was not possible to detect the implanted deuterium as it was below the detection limit.

Results

In Fig. 1 one can see the corresponding TSD spectra for two D\(^+\) implanted RB–SiC samples at 25 °C up to 1 × 10^{16} D/cm\(^2\) one implanted with 20 keV D\(^+\) and the other with 50 keV D\(^+\). The spectra are very similar being dominated by a structure formed by three bands between 450 and 800 °C. One can see that this group of bands shift to higher temperature as the implantation energy is increased. It is expected that there is not an important influence of HD molecules as the background pressure was better than 2 × 10^{-6} mbar.

The TSD spectra for two RB–SiC samples implanted with 20 keV D\(^+\) one at 25 °C and the other at 450 °C up to a dose of 1 × 10^{17} D/cm\(^2\) is shown in Fig. 2. In the case of the implantation at 25 °C the spectrum shows a prominent desorption around 450 °C together with another band around 600 °C similar to the band observed for the lower implantation dose shown in Fig. 1. In the case of the implantation at 450 °C the spectrum is similar for those shown in Fig. 1 for the samples implanted at lower dose but in this case the maximum for desorption is shifted from about 600 to 800 °C.

In Fig. 3 one can see the SIMS D profile for two 20 keV D\(^+\) implanted RB–SiC samples up to a dose of 1 × 10^{17} D/cm\(^2\), one at 25 and the other at 450 °C. Both implantations agree with the expected implantation range obtained from SRIM [6]. The quantity of deuterium measured as D is higher for the lower implantation temperature.

In Fig. 4 the SIMS D\(_2\) profile for two 20 keV D\(^+\) implanted RB–SiC samples up to a dose of 1 × 10^{17} D/cm\(^2\) at 25 °C both before and after being heated up to 1000 °C are shown in Fig. 5. One can see in Fig. 5 that the total integrated D quantity measured by SIMS after heating up to 1000 °C is about 30% lower than the total integrated D quantity measured by SIMS before heating.

Fig. 6 shows the SIMS D profile for a RB–SiC sample implanted with 20 keV D\(^+\) at 450 °C up to a dose of 1 × 10^{17} D/cm\(^2\) both before and after being heated up to 1000 °C. Nearly no change is observed after heating the sample up to 1000 °C.

In Fig. 7 it is shown the SIMS D\(_2\) profile for a RB–SiC sample implanted with 20 keV D\(^+\) at 25 °C up to a dose of 1 × 10^{17} D/cm\(^2\)
both before and after being heated up to 1000 °C. A clear reduction is observed after heating up to 1000 °C.

Fig. 8 shows the SIMS SiD profile for a RB–SiC sample implanted with 20 keV D+ at 450 °C up to a dose of $1 \times 10^{17}$ D/cm² both before and after being heated up to 1000 °C. A clear reduction is observed after heating up to 1000 °C in particular for those SiD which were deeper than the expected implantation range.

**Discussion**

Most of the deuterium thermal desorption occurs at about 600–800 °C for implantations at 25 °C as one can see in Figs. 1 and 2. This is in agreement with other works where deuterium desorption bands are reported also around within this range of temperatures [7,8]. Deuterium desorption at 600 °C was also observed in previous works where surface deuterium absorption at room temperature was carried out during 1.8 MeV electron irradiation [9]. In the case of deuterium implantation the desorption maximum occurs at higher temperatures as the implantation energy increases. A shift of 75 °C is observed to occur in Fig. 1 as the implantation energy is increased from 20 to 50 keV. As the samples were heated at 0.16 C/s it implies that a shift of 75 °C for the desorption temperature corresponds to a delay in deuterium release of 469 s. Assuming that this delay is due to the increase of about 200 nm in deuterium penetration for the higher implantation energy as
Deuterium is detected by SIMS either as D or as SiD but not as CD. This means that deuterium links to Si rather than to C. For the implantation at 25 °C both the D and SiD profile maxima agree with the maximum expected by SRIM calculation. However, in the case of the implantation at 450 °C one can clearly see that SiD can be found deeper than the expected range showing that deuterium thermal diffusion has occurred during implantation. Contrary to SiD, in the case of D profile for implantation at 450 °C no diffusion is observed indicating that this corresponds to deuterium trapped in deeper traps very likely associated to implantation damage.

The SIMS results after heating show that part of the deuterium stays within the samples after heating up to 1000 °C. In the case of the D profile a slight decrease is observed for the implantation at 25 °C after heating but no change at all is observed for the one implanted at 450 °C showing that these profiles correspond to deuterium trapped in stable sites probably associated to material damage consequence of displacement events. In the case of the SiD profile more noticeable changes are observed once the samples were heated up to 1000 °C in particular in the case of the sample implanted at 450 °C where a clear decrease in the profile is observed after heating in the region deeper than the implantation range where no implantation damage has occurred and deuterium cannot be trapped at implantation generated defects like vacancies.

When RB–SiC is deuterium implanted at higher doses the desorption spectra exhibits important differences depending on the implantation temperature. One expects that after 10^{17} D/cm² material damage due to implantation itself affects the deuterium trapping. Particularly when the implantation was carried out at 25 °C one can see in Fig. 2 that the desorption spectrum is clearly different to the spectra shown in Fig. 1 for the lower dose. For the implantation at 450 °C the TSD spectrum is similar to the ones in Fig. 1 but shifted to higher temperature. One expects that as the implantation temperature is increased, firstly, the deuterium diffusion is thermally enhanced so the implanted deuterium can move deeper into the sample and, secondly, part of the radiation damage produced by implantation itself is thermally annealed during implantation. Then the desorption spectra for higher dose at 25 °C is modified due to material damage meanwhile for the implantation at 450 °C the damage is dynamically annealed so the form of the spectrum is similar to the lower dose implantation for which the damage is low but the spectrum is shifted toward higher temperatures due to deeper deuterium thermal diffusion during implantation. Previous work showed important effects on the radiation induced deuterium absorption for SiC associated to damage production consequence of ion preimplantation [10]. Further work is in progress in order to evaluate the ion bombardment induced deuterium desorption from previously deuterium loaded SiC.

Conclusions

The observed shift of the deuterium desorption band for deuterium implanted SiC with increase of the implantation energy is due to both a higher penetration and a low diffusivity. The implanted deuterium is observed by SIMS measurements in two forms: either as D or as SiD indicating that the implanted deuterium links to silicon rather than to carbon. A great part of the implanted deuterium stays within the material after being heated up to 1000 °C. When the material is implanted at lower temperature the implanted deuterium is hardly thermally released due to stabilization in defects associated to damage produced during implantation meanwhile for higher implantation temperatures both thermal damage recovery and deuterium diffusion help to release the implanted deuterium.

predicted by SRIM [6] and as the implanted deuterium needs more time to reach the sample surface, then a rough estimation for deuterium diffusivity (D ≈ d²/t) is

\[ D \approx (200 \times 10^{-9})^2 / 469 \text{ m}^2/\text{s} = 8.5 \times 10^{-17} \text{ m}^2/\text{s} \]

The diffusivity value for SiC is \[ D = 9.8 \times 10^{-8} \exp(-1.89 \text{ eV/kT}) \] which gives a value at 700 °C of \[ 1.6 \times 10^{-17} \text{ m}^2/\text{s} \] within the same order of magnitude that the one estimated here. It is worth to point out that this desorption shift with implantation energy is observable because the deuterium diffusivity is particularly low for SiC.
Acknowledgments

The authors are indebted to J. Valle and F. Jiménez for their help in these experiments. The work has been directly supported by CIEMAT as part of the Spanish contribution to the EU/Japan BA activities.

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Please cite this article as: F.J. Sánchez et al., Trapping and thermal diffusion for energetic deuterium implanted into SiC, Nuclear Materials and Energy (2016), http://dx.doi.org/10.1016/j.nme.2016.03.007