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Radiation effects on the deuterium diffusion in SiO_2

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Abstract

Different oxides, mainly fused silica and aluminium oxide, are candidate materials to be used in different systems of ITER. Some applications require their use as confinement barriers for tritium and other radioactive products. The effect of radiation on diffusion mechanisms of fused silica is studied. To help clarify this phenomenon in a qualitative way, radiation effects on the behaviour of the implantation profile of deuterium are measured for fused silica. Deuterium has been introduced into the samples by 50 keV ion implantation and later on irradiated at different temperatures to induce diffusion. The modification of the implantation profile has been determined by Elastic Recoil Detection Analysis (ERDA) using Si ions. It is observed that high dose rate ionizing irradiation (over 100 Gy/s) induces changes in the D profile even at room temperature. No significant effects are observed for lower dose rate ionizing radiation effects or displacement radiation effects from 1.2 MeV Si ion irradiation.

1. Introduction

Heating, current drive and a number of diagnostics systems of ITER and, more generally, of fusion reactors, require insulator materials for different applications [1]. They will play a crucial role in some systems of the machine not only from the operational point of view but also for safety and control of the machine [2]. One of the most important materials is SiO_2 fused silica, to be used in optical and radio frequency diagnostics systems [3].

Many of these insulators will be exposed to the plasma particles that diffuse out from the plasma (deuterium, tritium and helium) that can deposit on the surface or even penetrate in the material. These ions will also appear inside the material due to nuclear reactions. The possible impact of the radiation fields should also be taken into account. One of the main concerns is on diffusion properties, including the impact of radiation fields.

The diffusion behaviour of hydrogen and its isotopes in insulator materials is not well characterized and its understanding is further complicated by the possible diffusion in different chemical forms (atomic or molecular) and the relative role of different trapping phenomena in defects or chemical reactions between the hydrogen and oxygen.

Values in the range of 10^{-7}–10^{-5} cm^2/s for the diffusion coefficient of hydrogen in silica were measured at temperatures between 750 and 1500 °C [4]. Although diffusion data for deuterium in fused silica are very scarce, it seems that the values for deuterium

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are in the same range [5]. These data indicate that H should be immobile at temperatures below 500–600 °C. This has been confirmed in implanted silica by measuring the amount of hydrogen that remains in the material as a function of temperature [6]. In this work it has been clearly observed that H is stable up to 400 °C.

In spite of this, some studies indicate that the creation and annihilation of defects are mediated by the movement of H ions [7,8]. From these data is has been concluded that H moves inside fused silica at temperatures well below room temperature. This apparent contradiction can be understood taking into account that the intrinsic diffusion coefficient of atomic hydrogen is expected to be very high [9], whereas the intrinsic diffusion of molecular hydrogen is much lower. The macroscopic diffusion measured in most of the experiments indicates that hydrogen diffusion in fused silica is mainly by molecular hydrogen. In addition, diffusion can be modified by the trapping of hydrogen in the silica network and the effects of chemical trapping at high temperatures due to the reactivity of the H ion [10].

This is further complicated by the presence of radiation. It has been shown that D implanted in Al_2O_3 diffuses during implantation at room temperature with an effective diffusion coefficient of about 10^{-12} cm^2/s, much greater that the expected diffusion coefficient (around 10^{-41} cm^2/s), suggesting a radiation-enhanced diffusion (RED) process [11].

RED occurs in insulating materials by different mechanisms and it has been observed in different materials and using different radiation sources [12–15]. Classical RED has been observed for O and other ions (Ti, Ca, Zn) in MgO and Al_2O_3. 'Classical' means that the observed behaviour can be explained using the theory developed for RED in metallic materials and it is controlled by the creation of an increased concentration of defects during or after irradiation. It can be reduced by the recombination of radiation induced vacancies and interstitials [13,15] or by the presence of vacancy clusters [14]. But, on the other hand, ionization induced RED is also observed [16–18]. Ionization induced valence changes for impurities and charged vacancies cause changes in the corresponding defect activation energy for diffusion.

For fusion applications, the possibility of radiation-enhanced tritium diffusion either directly through the window or feedthrough barrier, or via the metal/ceramic interface represents a safety hazard.

This work describes the results of some experiments intended to confirm radiation-enhanced diffusion phenomena of light ions in insulator materials as well as to clarify the role of the different types of radiation. The effect of different irradiation sources on the shape of a concentration profile of deuterium in a fused silica sample is measured. The concentration profile induced by low energy ion implantation is of interest because it is similar to the one that can be found in a fusion reactor. With these experiments it will be possible to explore the effect of very different dose rates of ionizing radiation as well as displacement effects on the D profile.

2. Experimental

The samples used were commercial natural silica Infrasil 301 (Heraeus, Germany) with relatively low OH contents (around 10 ppm). D implantations at room temperature were made using different ion implantation machines at dose rates between 3×10^{12} and 6×10^{13} ions/cm^2 s up to doses from 5×10^{16} to 5×10^{17} ions/cm^2. All the implantations are made with ions of energy around 50 keV.

Gamma irradiations were made at room temperature using a ^{60}Co gamma source (NAYADE installation at CIEMAT) and electron irradiations were made in a 2 MeV Van de Graff electron accelerator at CIEMAT.

The D profile was characterized using Elastic Recoil Detection Analysis (ERDA). ERDA has been widely used for quantitatively profiling hydrogen isotopes. The composition profile with depth was obtained by ERDA using the IBA facility at Centro de MicroAnalisis de Materiales in Madrid (CMAM). Si ion beams with energies in the range of 20–35 MeV were used. The samples were mounted on a sampler holder, attached to a goniometer which assured an angle of 75° between the target surface normal and the incident beam. An ion-implanted silicon detector was placed at a scattering angle of 30°, behind a 13 μm thick Mylar absorbing foil. This stopped all silicon scattered particles but allowed recoil atoms from the sample lighter than Si to pass through. Spectra have been simulated and quantified using computer programs SIMNRA [19] and RBX [20]. The same beam, with energies between 1 and 25 MeV has been used for ion irradiations at room temperature.

The use of different radiation sources allows the determination of the role of very different radiation

effects and dose rates. It is well known that primary radiation damage can be classified as arising from two main effects: ionizing effects, that induce the creation of a huge number of electron–hole pairs in the material, and displacement damage that induces the creation of defects associated with vacancies and interstitials. The radiation sources used allow us to reach very different ratios of these two different radiation mechanisms. The ^{60}Co source induces mainly ionizing effects with a low dose rate (around 10 Gy/s) in the studied materials. The 2 MeV electron accelerator induces mainly ionizing effects with a dose rate in the range of 100–10 000 Gy/s. The Si irradiation at the CMAM accelerator yields ionizing dose rates around 10^8 Gy/s or displacement rates around 4×10^{20} atoms/s cm^3 using ions of 30 MeV or 1.2 MeV respectively, in the region in which the D ions are concentrated. These numbers have been calculated using the SRIM 2003 code [21] for a depth of 500 nm, in the range of the 50 keV D implanted ions.

3. Results and discussion

As has been previously mentioned, the main objective of the work was to determine in a qualitative way, if different kinds of irradiation induce different changes in the D distribution. The main results are described in the following paragraphs.

3.1. Gamma irradiation effects

Several samples previously implanted with 50 keV D ions to doses around 5×10^{16} ions/cm^2 were irradiated with a ^{60}Co source. The irradiations have been made at room temperature, in a flowing N_2 atmosphere up to a total dose of 0.8 MGy. After implantation and/or irradiation, samples were characterized using 30 MeV ERDA. Fig. 1 shows a representative example of the obtained results. The ERDA spectra of an as-received SiO_2 grade, a sample implanted with 50 keV ions and a similar sample after gamma irradiation can be observed. In this figure, x-axis is proportional to the energy of the scattered particle and the y-axis to number of counts in each energy range.

In the unirradiated sample the observed spectra is composed of a sharp peak around channel 450, related to the presence of H in the surface and a continuous increase for channels of low energy, which are due to the O in the sample. For the other samples, an increased number of counts for channels 400–600 are observed. This is related to the D implanted in the sample. The fit using SIMNRA code agrees with the deuterium content and distribution expected taking into account the implantation. This fit (as all the others mentioned below) were made fitting the experimental spectra to a target-sample made of up to 10 layers of the same thickness composed of Si, O and D with different concentrations. An additional thin layer at the surface also contains H. The comparison between the as-implanted and the gamma irradiated samples clearly shows that gamma irradiation does not induce any change in the ERDA spectrum.

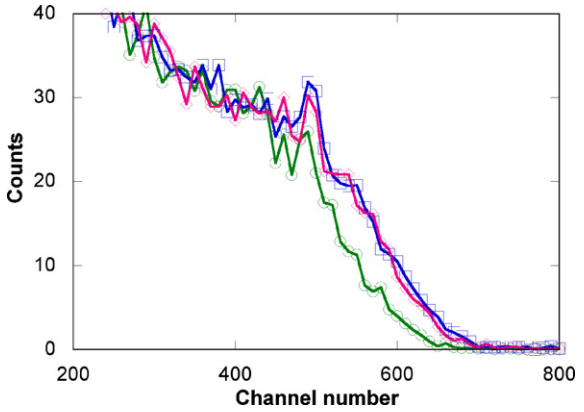

Fig. 1. 30 MeV Si ERDA spectra for SiO_2 samples before (○) and after D implantation up to a total dose around 5×10^{16} ions/cm^2 with 50 keV ions (□) and after gamma irradiation at room temperature up to a total dose around 0.8 MGy (△).

3.2. Electron irradiation effects

A sample implanted with 50 keV D ions up to 5×10^{16} ions/cm^2 was irradiated with 1.8 MeV electrons at a current of 10 μA (an equivalent ionizing dose rate of 2.5×10^4 Gy/s and displacement rate around 10^{-10} dpa/s) at 320 °C up to a dose of 220 MGy.

Fig. 2 shows the ERDA spectra before and after the electron irradiation, compared with the ERDA spectrum of an as-received sample. In this case, it can be clearly observed that the contribution of the deuterium ions disappears after the electron irradiation, indicating that most of the implanted D diffuses out of the sample. At this point it should be emphasized that, according to results in [6], D implanted in SiO_2 is stable up to temperatures over 400 °C. This result strongly suggests that high dose rate ionizing radiation-enhances the diffusion of D ions, at least at temperatures around 300 °C. The

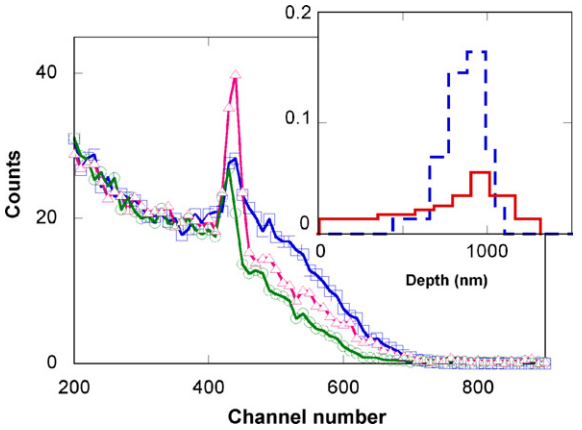

Fig. 2. 30 MeV ERDA spectra for SiO_2 samples before (○) and after D implantation up to a total dose around 5×10^{16} ions/cm^2 with 50 keV ions (□), and after electron irradiation at 320 °C up to a total dose around 220 MGy (△). Inset: Deuterium concentration (10^{22} ions/cm^3) as a function of the distance to the surface after D implantation (dotted line) and after electron irradiation (continuous line).

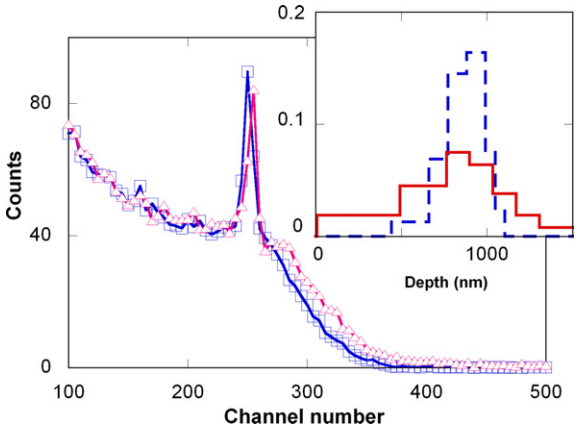

Fig. 3. 30 MeV ERDA spectra for SiO_2 samples implanted with 50 keV D ions up to a total dose around 5×10^{16} ions/cm^2 before (□) and after (△) electron irradiation at room temperature up to a total dose around 9 MGy and a dose rate of 420 Gy/s. Inset: Deuterium concentration (10^{22} ions/cm^3) as a function of the distance to the surface after D implantation (dotted line) and the electron irradiation (continuous line).

inset in Fig. 2 shows the D concentration (in 10^{22} ions/cm^3 units) as a function of the distance to the surface before and after the electron irradiation. A clear broadening of the D distribution, induce by the electron irradiation, can be observed. The total contents of D can be estimated by integration of these curves and a clear decrease (around 40%) of the total D in the sample is also observed after electron irradiation.

In order to clarify this point, electron irradiation of a similar sample was carried out at room temperature. Irradiation was made at a dose rate around 420 Gy/s up to a total dose of 9 MGy. Fig. 3 shows the ERDA spectra before and after the electron irradiation. It can be observed that the D contribution is lowered and shifted towards the surface after irradiation, confirming electron irradiation is able to modify the D profile even at room temperature. The inset in Fig. 3 also shows the D concentration (in 10^{22} ions/cm^3 units) as a function of the distance to the surface before and after the room temperature electron irradiation. Again, a clear broadening of the D distribution, induce by the electron irradiation, can be observed, but in this case the total content of D before and after the electron irradiation is the same.

3.3. 25 MeV Si ion irradiation effects

Samples implanted with 50 keV D ions up to 1.5×10^{17} ions/cm^2 were irradiated with 25 MeV Si^{4+} ions up to a total dose around 25 μC at room temperature. According to the calculations made using SRIM2003, the irradiation with ions of this energy allows transferring a huge quantity of ionizing energy (around 10^8 Gy/s) in the region in which the D ions are concentrated. The 25 MeV ERDA spectra, taken before and after the Si ion irradiation, can be observed in Fig. 4. It should be noted that these spectra are taken at a different energy compared with the spectra of the other figures. In these spectra the channels around 500 are related to the presence of H in the surface, whereas the channels related to D are between 600 and 1200. It can be clearly observed that the D distribution widens and the total amount of D in the sample decreases as a consequence of the ion irradiation. This is confirmed by the results shows in the inset in Fig. 4. It shows the D concentration (in 10^{22} ions/cm^3 units) as a function of the distance to the surface before and after the ion irradiation. In this case a clear broadening of the D distribution, as well as a decrease of the total D concentration is observed induce by the ion irradiation. This figure also shows that the D distribution of the sample after implantation (and before the ion irradiation) is different to the one obtained in previous figures. The peak of the D concentration appears at a depth of 600 nm, whereas in the previous cases it appears around 900 nm. This effect is not clearly understand up to now but maybe is related to the increased D implantation dose

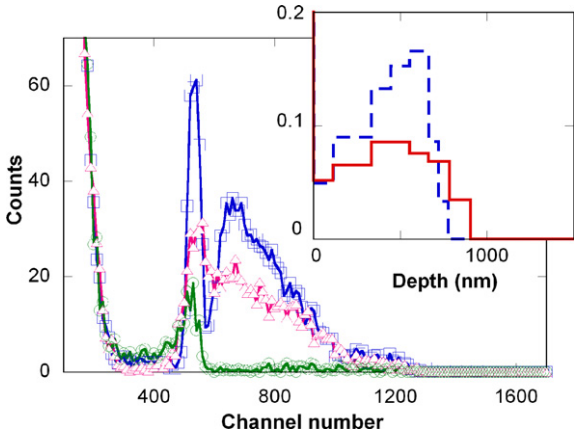

Fig. 4. 25 MeV ERDA spectra for SiO_2 samples. (○) as-received and implanted with 50 keV D ions up to a total dose around 5×10^{16} ions/cm^2 before (□) and after (△) 25 MeV Si ion irradiation at room temperature up to a total dose around 30 μC. Inset: Deuterium concentration (10^{22} ions/cm^3) as a function of the distance to the surface after D implantation (dotted line) and after ion irradiation (continuous line).

(1.5×10^{17} ions/cm^2 to be compared with 5×10^{16} ions/cm^2 in the other samples).

3.4. 1.2 MeV Si ion irradiation effects

Samples implanted with 50 keV D ions up to 1.5×10^{17} ions/cm^2 were irradiated with 1.2 MeV Si^{+1} ions up to a total dose around 30 μC. According to the calculations made using SRIM2003, irradiation with ions of this energy creates a huge number of displacement defects in the region in which the D ions are concentrated and, at the same time, the ionizing dose rate is much smaller. 30 MeV Si ERDA spectra were taken before and after the Si ion irradiation. The results can be found in Fig. 5. The comparison between the as-implanted and the ion irradiated samples indicates that displacement irradiation does not induce any change in the ERDA spectrum.

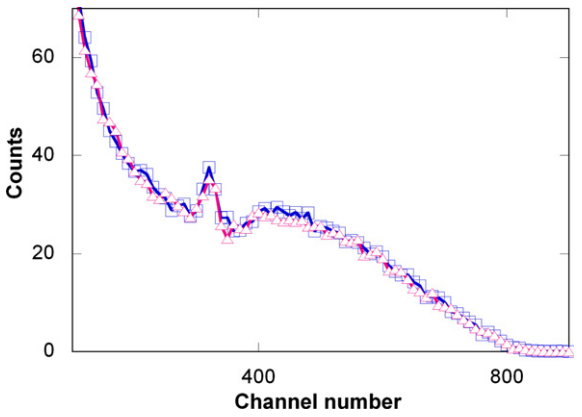

Fig. 5. 30 MeV ERDA spectra for SiO_2 samples implanted with 50 keV D ions up to a total dose around 1.5×10^{17} ions/cm^2 before (□) and after 1.2 MeV Si ion irradiation at room temperature up to a total dose around 30 μC (△).

4. Conclusions

In summary, it has been found that electron irradiations in the 0–400 °C temperature range, as well as high dose rate ionising radiation from Si ions induce a broadening of the profile of implanted D in fused silica. On the contrary low dose (and low dose rate) gamma irradiation does not induce any change in the D concentration and profile. This suggests that under ionizing irradiation diffusion coefficients and trapping probabilities of D are modified compared with those that can be observed without irradiation. The ionizing radiation dose rates should be at least in the 100 Gy/s range.

On the other hand, no effect on the D distribution has been found as a consequence of the increased concentration of defects induced by displacement damage. The possible role of these defects may be masked by the important effects associated with ionizing radiation. More work is needed to further confirm these results for different irradiation doses, different temperatures and other materials.

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