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Depth distribution of deuterium atoms and molecules in beryllium implanted with D ions

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Abstract

In-depth concentration profiles of deuterium atoms and molecules in beryllium implanted with 9 keV D ions to fluences, Φ, in the range from 6×10^{19} to 9×10^{22} D/m^2 at temperatures, T_{irr}, of 300 and 700 K have been determined using SIMS and RGA (residual gas analysis) measurements in the course of surface sputtering. The microstructure of implanted specimens was studied by TEM. Implanted deuterium is retained in Be matrix in the form of both D atoms and D_2 molecules. The total amount of gas captured within the sub-surface layer of ~ 700 nm in thickness as a result of implantation at 300 and 700 K reaches 4×10^{21} and 1×10^{21} D/m^2, correspondingly. The ratio of deuterium quantities retained in the form of atoms and molecules, Q_D:Q_{D_2}, varies from 1:3 for $T_{irr} = 300$ K to 1:4 for $T_{irr} = 700$ K. At $T_{irr} = 300$ K the concentration of D_2 molecules at the depth of the ion mean range reaches its maximum of 4×10^{27} molecules/m^3 at $\Phi \approx 2 \times 10^{21}$ D/m^2. The molecules are present in tiny bubbles which show a tendency toward interconnection at higher fluences. At $T_{irr} = 700$ K, along with relatively small facetted bubbles (near the very surface), large oblate gas-filled cavities and channels forming extended labyrinths appear and they accumulate most of the injected gas. The maximum D_2 concentration in the latter case is of 1×10^{27} molecules/m^3. The high concentration of D atoms in the ion stopping zone after implantation at $T_{irr} = 300$ and 700 K (about 2×10^{27} and 1×10^{27} atoms/m^3, respectively) is attributed to deuterium (i) trapped in radiation vacancies, (ii) adsorbed on the walls of bubbles and channels and (iii) bonded to/by BeO formed on the surface and present in the form of metallurgical inclusions in the bulk.

Keywords: Wall particle retention; Low Z wall material

1. Introduction

Present concepts for the ITER consider Be as a candidate first-wall material [1]. The behavior of implanted hydrogen isotopes in Be is of great concern for the fuel recycling and for the tritium inventory in the wall tiles.

Trapping characteristics of hydrogen implanted into beryllium have been reviewed by Wilson et al. [2]. The most systematic studies of hydrogen retention have been performed by Wampler [3,4], Möller et al. [5] and Kawamura et al. [6]. At irradiation temperature, $T_{irr} = 300$ K and low fluences, Φ, 100% of deuterium implanted into Be is trapped, while at high Φ the maximum gas concentration reaches 0.31 ± 0.05 D/Be [3,6,7]. Wampler suggested two types of traps for D atoms with detrapping energies of 1 eV and 1.8 eV, correspondingly, and put forward an idea about the formation of deuterium bubbles [3]. At low Φ implanted D atoms were believed to be trapped in vacancies, while at high Φ deuterium was concluded to precipitate into gas bubbles [4]. Having in mind a very low solubility of hydrogen in Be [8,9], Pemsler and Rapperport [10] have shown using optical microscopy that, presumably, H_2 filled cavities were formed in this metal implanted with 7.5 MeV protons and annealed at 623 K and higher. Blister formation due to hydrogen ion implantation was reported in Ref. [11]. Thus, if even not direct, some facts in the literature pointed out that implanted hydrogen could reside in Be not only as separate atoms, but also in the form of molecules.

In the frames of the present investigation concentration profiles of deuterium accumulated in the form of D atoms

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and D_2 molecules were reliably estimated using SIMS and RGA (residual gas analysis) methods for Be implanted with 9 keV D ions up to different fluences at 300 and 700 K. Relevant results presented in this paper made it possible to get a deep insight into processes accompanying gas swelling and other related phenomena in Be under D ion implantation [12].

2. Experimental

The hot-pressed beryllium S-65B (Brush Wellman) containing about 1 wt% of BeO was used [13]. Prior to implantation all samples were polished mechanically and electropolished. According to the data of electron probe microanalysis [14], the thickness of the surface oxide layer was less than 6 nm.

Experiments were performed in a special two-chamber UHV system with a typical background pressure better than 1×10^{-7} Pa. The samples were implanted in the first vacuum chamber with mass-separated 18 keV D_2^+ ions at $T_{irr} = 300$ and 700 K up to Φ in the range from 6×10^{19} to 9×10^{22} D/m^2. In order to achieve a uniform implantation over the whole bombardment area, the ion beam of 0.5 mm in diameter was swept electrostatically in the x and y directions over an area of 3.0×4.3 mm^2. Up to $\Phi = 10^{21}$ D/m^2 the ion flux density, j, was $(8–10) \times 10^{18}$ D/m^2 s, while for $\Phi > 10^{21}$ D/m^2, j came up to $(2.8–3.0) \times 10^{19}$ D/m^2 s. During measurements of the ion beam current a positive bias of 15 V was applied to the target to suppress the secondary electron emission.

After implantation, Be samples were transferred in vacuo into the second analytical chamber for SIMS measurements of H^- and D^- secondary ion yields and RGA measurements of the partial pressures of D_2 and HD molecules in the course of sputtering of the surface with 4 keV Ar^+ ions [15]. All measurements were made at 300 K, 1–2 days after ion implantation. The use of two quadrupole mass spectrometers (QMS) made it possible to register SIMS and RGA signals simultaneously. Partial pressures of HD and D_2 molecules evolved were determined taking into account the background intensities of masses 3 and 4, which were measured with the Ar ion beam switched off. The sputtering rate of Be was estimated with an accuracy of 20% as a ratio of the depth of a crater produced by sputtering on the surface to the sputtering time.

We attribute the appearance of the SIMS D^- signal to the existence of separate D atoms within the matrix. When recording D atom depth profiles a special method was undertaken to minimize the influence of oxygen atoms on the surface on the D^- yield. It consisted in the simultaneous monitoring of the D^-/H^- signal ratio, as a correction factor to the experimental D^- yield. The underlying assumption is that during sputtering at constant parameters of the Ar ion beam, protium yield depends solely on vacuum conditions. Usually, the H^- yield is first relatively high until a layer of surface oxide is sputtered fully and then remains constant with an accuracy of 20%.

Due to recombination of sputtered D atoms with H atoms adsorbed on the inner surfaces of the vacuum chamber, the dependencies of the HD RGA signal on the depth are reminiscent of those of the D^- SIMS signal. A cause of the D_2 signal appearance seems to be the recombination of D atoms as well as the direct release of D_2 molecules from the sputtered layers. In order to distinguish the recombination and molecular fractions, the HD and D_2 RGA signals were measured simultaneously. We assume that in the absence of the molecular fraction the intensity of the D_2 signal should be proportional to the square of the intensity of the HD signal. Such a proportionality is observed in fact after D ion irradiation of Be at 300 K up to $\Phi < 1 \times 10^{20}$ D/m^2. The coefficient of the proportionality, K, depends on vacuum conditions and has much in common with that obtained in our earlier experiments [15]. Regarding K as a constant during sputtering in RGA measurements, one can determine the intensity of the signal I_{mol} caused solely by the release of molecular deuterium:

$$I_{mol} = I_{D_2} - K(I_{HD})^2,$$

where I_{D_2} and I_{HD} are the experimentally measured intensities of the D_2 and HD RGA signals, respectively. In practice, the I_{HD} intensity is 3–6 times lower than I_{D_2} intensity.

The D-atom concentration was determined by comparison of the integral SIMS signal (all over the implantation depth) with the total amount of deuterium in the sample implanted at 300 K to $\Phi = 6.0 \times 10^{19}$ D/m^2. For the above fluence Be retains 100% of implanted atoms [5] and the value of I_{mol} is zero. The amount of D_2 molecules released under sputtering was estimated from a I_{mol} signal value taking into account the sensitivity of RGA QMS and a known pumping speed. The total error of RGA QMS calibration was about 40%.

The microstructure of D ion implanted Be was studied in analytical TEM EM-400T operated at 120 kV. Hot isostatically pressed Be TIP-30 (Bochvar Institute, Moscow) with BeO content of ~ 2 wt% [16] was taken for carrying out these studies. The samples were implanted with 20 keV D_2^+ ions in the same vacuum system up to different fluences at 300 and 700 K. The detailed information on TEM specimen preparation and methods of TEM data processing are given in Ref. [12].

3. Results and discussion

Depth profiles of deuterium trapped in the form of D atoms and D_2 molecules at $T_{irr} = 300$ K are shown in Fig. 1. At $\Phi < 2 \times 10^{21}$ D/m^2 the maximum of the D atom distribution (Fig. 1a) is at about 180 nm which is in agreement with the mean projected range, $\bar{R}_p$, calculated

according to the power-law fit due to Leblanc and Ross [17]. With the fluence increase the D atom concentration, C_D, reaches about 2×10^{27} atoms/m^3 and practically does not change any more. A significant feature is a much higher value of C_D near the surface compared to that in the bulk. The total amount of atomic deuterium in the sub-surface layer of ~ 700 nm in thickness (areal density) increases slowly with the fluence and at $\Phi \cong 1 \times 10^{23}$ D/m^2 reaches its saturation level of 1×10^{21} D/m^2 (Fig. 2).

Analysis of depth profiles of molecular deuterium shows that the formation of D_2 molecules in the ion stopping zone starts at $\Phi \geq 1.5 \times 10^{20}$ D/m^2 (Fig. 1b) that is at $C_D \geq 1$ at% (Fig. 1a). The areal density of molecules increases nonlinearly with a fluence (Fig. 2). While C_D (at the depth of $\bar{R}_p$) only doubles when increasing Φ from 1.5×10^{20} to 1.9×10^{21} D/m^2 (Fig. 1a), the concentration of molecules, C_{D_2}, increases more than an order of magnitude reaching its maximum value of 4×10^{27} molecules/m^3 (Fig. 1b). The further fluence increase leads to the broadening of C_{D_2} profile. At $\Phi = 9 \times 10^{22}$ D/m^2 the areal density of deuterium trapped in the form of D_2 reaches about 3×10^{21} D/m^2 (Fig. 2).

At maximal Φ and $T_{irr} = 300$ K the concentration of deuterium present in both states (D atoms and D_2 molecules) at the depth of $\bar{R}_p$, and its total amount trapped within the sub-surface layer are estimated to be about 0.1 D/Be and 4×10^{21} D/m^2, respectively. The latter value correlates well with that reported in Ref. [5]. On the other hand, the concentration of 0.1 D/Be derived from our experiments is lower than the values determined in Refs. [3,6,7]. This discrepancy is attributed to the fact that the deuterium accumulated in Be has a tendency for a partial escape after the implantation completion. Within 14 h its concentration falls down from 0.36 to 0.24 D/Be, as it was observed in Ref. [6]. In the present work SIMS and RGA measurements were carried out in 1–2 days after ion implantation which can serve a plausible explanation for the magnitude of D/Be ratio value we obtained.

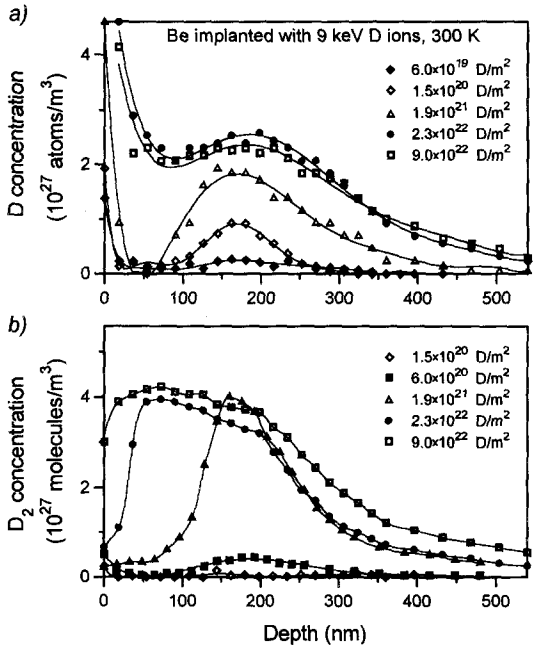

Fig. 1. Concentration profiles of deuterium trapped as D atoms (a) and in the form of D_2 molecules (b) in Be implanted with 9 keV D ions at 300 K.

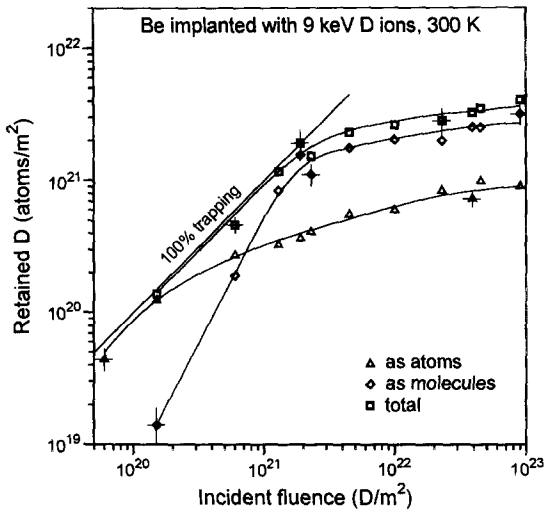

Fig. 2. Fraction quantities of deuterium trapped as D atoms and D_2 molecules and the total amount of deuterium in the ion stopping zone of Be implanted with 9 keV D ions at 300 K as a function of fluence. The lines are drawn to guide the eye.

Quite different features of deuterium accumulation were found for $T_{irr} = 700$ K (Fig. 3). Depth profiles of C_D do not concur with the ion projected range distributions and are characterized by a gradual decrease with the depth. With the fluence increase, C_D grows practically without any changes in C_D profile shapes, but at $\Phi > 1 \times 10^{21}$ D/m^2 it decreases slightly within a depth interval up to 250 nm (Fig. 3a). Similar to the case of $T_{irr} = 300$ K, at $T_{irr} = 700$ K a high value of C_D is built up near the surface as well. The maximal concentration C_D in the ion stopping zone (excluding surface layers) does not exceed 8×10^{26} atoms/m^3 (Fig. 3a), whereas the total amount of D atoms within the sub-surface layer reaches 2×10^{20} D/m^2 (Fig. 4).

In contrast to $T_{irr} = 300$ K, an active formation of D_2 molecules at 700 K occurs already at Φ about 9×10^{19} D/m^2 (Fig. 3b). For fluences up to about 7×10^{20} D/m^2 the shape of C_{D_2} profiles agrees with that of the ion projected range distributions. At higher Φ the shape of D_2 profiles undergoes transformations, namely C_{D_2} decreases by about 30% at the depth of $\bar{R}_p$. The C_{D_2} maximum of 1×10^{27} molecules/m^3 appears at the depth of 50–100 nm (Fig. 3b). The amount of deuterium accumulated in the

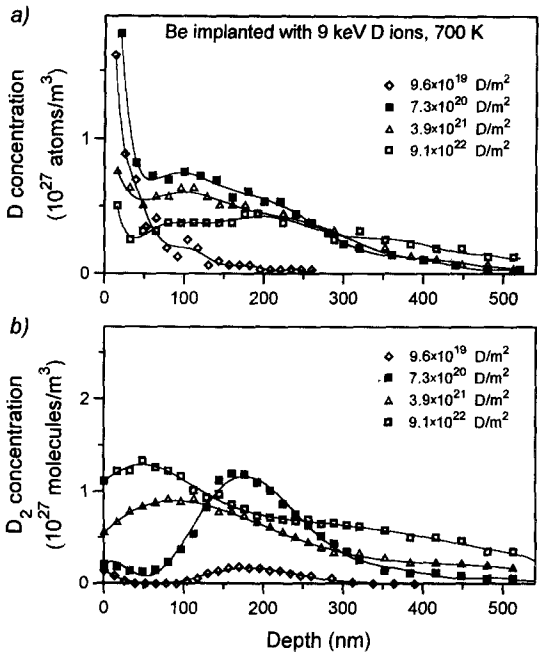

Fig. 3. Concentration profiles of deuterium trapped as D atoms (a) and in the form of D_2 molecules (b) in Be implanted with 9 keV D ions at 700 K.

form of D_2 within the sub-surface layer reaches 8×10^{20} D/m^2.

After $T_{irr} = 700$ K the maximal total concentration of deuterium (D atoms and D_2 molecules) in the ion stopping zone was estimated to be ≈ 0.03 D/Be. The total amount of trapped deuterium present in the two states appeared to

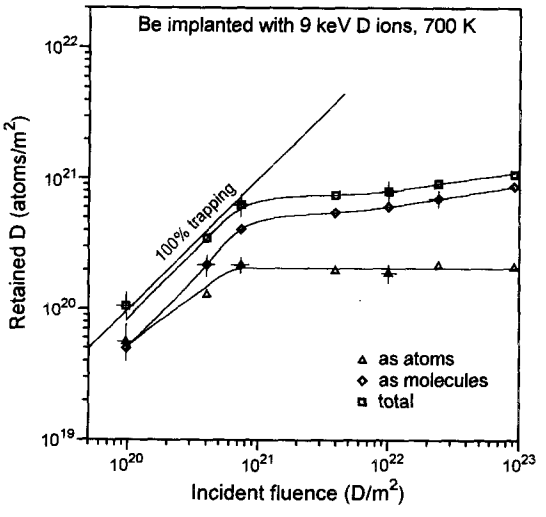

Fig. 4. Fraction quantities of deuterium trapped as D atoms and D_2 molecules and the total amount of deuterium in the ion stopping zone of Be implanted with 9 keV D ions at 700 K as a function of fluence. The lines are drawn to guide the eye.

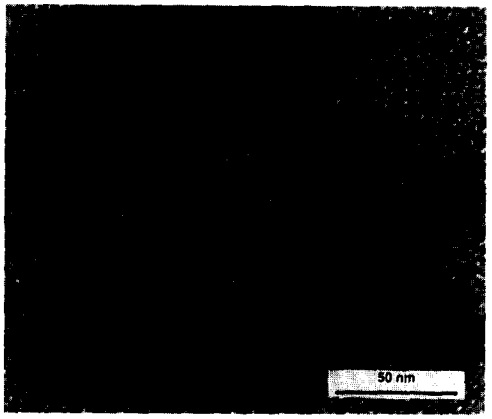

Fig. 5. Deuterium bubbles in Be blister cap after irradiation with 10 keV D ions up to $\Phi = 4 \times 10^{21}$ D/m^2 at 300 K.

be about 1×10^{21} D/m^2 (Fig. 4), this value is in good agreement with that reported in Ref. [5].

The application of TEM made it possible to relate the appearance of D_2 molecules in the ion stopping zone to the formation of D_2 gas bubbles and cavities. Relatively small ($r_b \sim 1$ nm) and highly pressurized D_2 bubbles develop under D ion implantation at $T_{irr} = 300$ K (Fig. 5). When the total deuterium concentration in the ion stopping range reaches about 0.08 D/Be atomic ratio, bubble interconnection begins and extends towards the surface with increasing fluence. In samples implanted with D ions at $T_{irr} = 700$ K the most of molecular gas is found in large oblate and flattened-out cavities forming at a depth of R_p complicated labyrinth systems which interact with the outer surface (Fig. 6). A minor part of captured D_2 gas appears to be within smaller in size well facetted gas filled cavities found closer to the surface. The D_2 depth profiles measured after $T_{irr} = 300$ and 700 K (Fig. 1b and Fig. 3b) reflect the processes of gas cavity evolution with fluence increase. For instance, the coalescence of gas bubbles under D ion implantation at 700 K and the development of interconnected channels explain the D_2 profile transformations at Φ above 7×10^{20} D/m^2 (Fig. 3b).

A detailed information on the defect structure of Be due to D ion implantation under different conditions together with an analysis of various related phenomena observed by means of TEM, SIMS, RGA and TDS is given in Ref. [12].

As to D atoms, we believe that at $T_{irr} = 300$ K they are trapped, first in radiation vacancies as it was proposed in Refs. [3,4] and checked experimentally in Ref. [12]. At $T_{irr} = 700$ K deuterium-vacancy complexes are unstable [3,4,12]. A relatively high concentration of D atoms in the surface oxide layer at $T_{irr} = 300$ and 700 K can be associated with the formation of beryllium hydroxide as a consequence of the reaction between D atoms and BeO [18]. A radiation enhanced growth of BeO surface layers (with a radiation modified microstructure) revealed in Ref. [12]

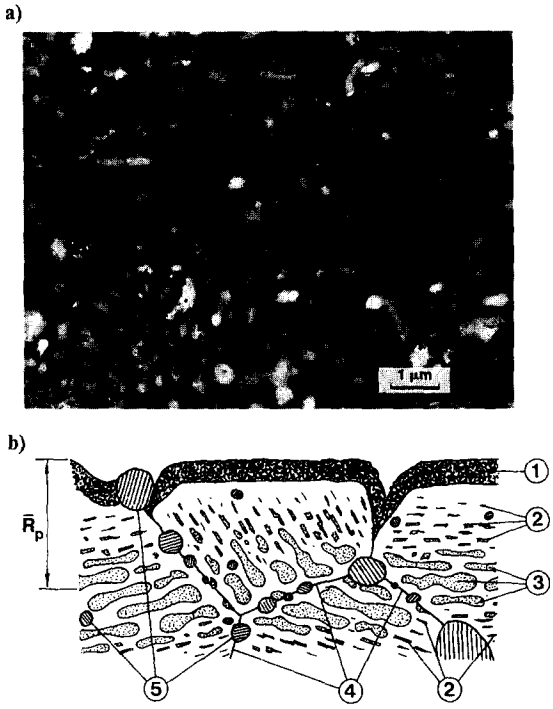

Fig. 6. Deuterium bubbles and cavities in Be after irradiation with 10 keV D ions up to $\Phi = 4 \times 10^{21}$ D/m^2 at 700 K (a) and a cross-sectional scheme of the near-surface microstructure for $T_{irr} \geq 500$ K and $\Phi \geq 2 \times 10^{21}$ D/m^2 (b): (1) BeO oxide surface layer, (2) small prismatic D_2 bubbles, (3) large oblate D_2 cavities, (4) grain boundaries (subjected to etching at $T_{irr} \geq 700$ K) and (5) metallurgical BeO precipitates.

may provide for the further increase of the amount of D atoms captured near the surface. Obviously, BeO inclusions in the bulk are strong traps for D atoms too. Another source of D atoms in D implanted Be at $T_{irr} = 300$ and 700 K is deuterium adsorbed on bubble and cavity walls [12,19]. Rough destructions in the near-surface layers and uncovering of interconnected wide channel systems occurring at $T_{irr} = 700$ K are possibly the reasons of the non-monotonous evolution of C_D and C_{D_2} profiles with the fluence increase at $\Phi \geq 3 \times 10^{21}$ D/m^2 (Fig. 3).

4. Conclusions

The depth concentration profiles of deuterium trapped in Be matrix as separate D atoms and D_2 molecules after the D ion implantation at 300 and 700 K were experimentally determined. It was shown that the total amount of deuterium (D atoms and D_2 molecules) retained in Be after the ion implantation at 300 K is four times as large as that after 700 K. It was also established that the ratio of deuterium quantities in these two states, Q_D:Q_{D_2}, varies from 1:3 for the implantation at $T_{irr} = 300$ K to 1:4 for that at $T_{irr} = 700$ K.

The appearance of molecular deuterium in D implanted Be is related to the formation of deuterium filled bubbles and cavities. A high concentration of D atoms in the near-surface layers is attributed to (i) the trapping of D atoms in radiation vacancies, (ii) deuterium adsorption on bubble and cavity walls and (iii) the bonding of D atoms to BeO oxide present as a surface oxide layer and as metallurgical inclusions in the bulk, which might result in the formation of beryllium hydroxide.

Acknowledgements

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