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Deuterium accumulation in beryllium oxide layer exposed to deuterium atoms

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Abstract

The interaction of deuterium atoms with beryllium TIP-30 was studied at temperatures of 340, 500 and 740 K. After D atom exposure, the depth distributions of deuterium atoms and molecules in Be were measured using combined Secondary Ion Mass Spectrometry (SIMS) and Residual Gas Analysis (RGA) methods. It was shown that deuterium is mainly accumulated in the oxide layer although long tails are also observed. Deuterium is retained in two states – atomic and molecular forms. The amount of trapped deuterium in samples decreases during the sample storage in vacuum or air at room temperature. The results were explained by the chemical bonding of D atoms in BeO oxide with beryllium hydroxide formation and the trapping of deuterium molecules in bubbles which are formed at growth defects in the oxide layer. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

During recent years many publications have been devoted to the interaction of hydrogen isotopes with beryllium, one of the possible advanced plasma-facing materials for fusion devices. Many works were done using ion or plasma irradiation. But it is also of interest to study the interaction of thermal or subthermal hydrogen (deuterium) atoms with beryllium because the neutral charge-exchange atoms compose a significant part of the particle flux which interacts with plasma-facing materials in fusion devices. In addition, such experiments may throw light upon peculiarities of the retention and release of hydrogen isotopes in/out of the oxide layer usually present on Be surfaces.

Recently, the deuterium retention in beryllium exposed to D atoms has been studied using Elastic Recoil Detection (ERD) method [1]. It was shown that some characteristics of the deuterium retention in Be in this case are similar to those for Be irradiated with D ions [2]. However, the mechanisms of deuterium trapping in both cases are probably different. In this work we have

continued the study of the interaction of D atoms with Be to determine the mechanism of deuterium trapping in a beryllium oxide layer.

2. Experimental

Beryllium TIP-30 manufactured in the Bochvar Institute by hot isostatic pressing was used (content of BeO was about 2 at%). A plasma source with heated cathode was used to produce deuterium atoms. The base vacuum was 1.33×10^{-4} Pa. A Be sample on a holder was located near the plasma column and a positive potential of +80 V was applied to the holder during D atom exposure to screen the sample from positive D ions. Therefore, the sample was mainly exposed to atomic deuterium and electron fluxes. The flux of incident D atoms was estimated to be $\sim 10^{16} \text{ cm}^{-2} \text{ s}^{-1}$ [3]. Molecular deuterium at a pressure of 5×10^{-1} Pa (the deuterium pressure in the chamber during the exposure) also interacted with the sample.

Depth profiles of D atoms and D₂ molecules were determined by SIMS (Secondary Ion Mass Spectrometry) measurements of H⁻ and D⁻ secondary ion yields and RGA (Residual Gas Analysis) measurements of the partial pressures of D₂ and HD molecules were made in the course of sputtering the sample surface with 4 keV

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Ar⁺ ions. (The use of two quadrupole mass spectrometers gives the possibility to register SIMS and RGA signals simultaneously.) A detailed description of the profiling method is given in Ref. [2].

3. Results and discussion

The depth profiles of trapped deuterium in Be samples after 1 h exposure to D atoms at temperatures 340, 500 and 740 K are shown in Fig. 1(b). One should note that the profiles of all deuterium measures by combined SIMS and RGA methods coincide with the profiles measured by ERD [1]. Simultaneously the oxygen profiles were measured in these samples which are given in Fig. 1(a). The comparison of the profiles of Fig. 1(a) and (b) give the possibility to conclude that oxygen profiles correlate quite well with trapped deuterium profiles. It means that the trapped deuterium is mainly accumulated in the beryllium oxide layer. Therefore, the presented results describe the features of deuterium accumulation and retention in beryllium oxide but not in the Be matrix.

The deuterium content in samples is changed non-monotonically when the sample temperature during the exposure increases. At 340 and 500 K the deuterium

contents are approximately the same $\sim 1 \times 10^{16}$ D/cm² and do not depend on the temperature. But at 740 K the content increases to 2.35×10^{16} D/cm². At the same time the depth of deuterium spreading increases up to 200–250 nm whereas at low temperatures it is equal to ~ 100 nm.

Fig. 1(b) shows the distribution of total deuterium content which was obtained by summation of the depth profiles of D atoms and D₂ molecules. Both these profiles are given in Fig. 2 for the samples exposed to D atoms at 740 K for 1 and 4 h. It is possible to conclude the following:

1. The total amount of trapped deuterium grows when the exposure time is increased. After 1 h exposure it was equal to 2.35×10^{16} D/cm² whereas after 4 h it was 8.9×10^{16} D/cm².

2. There are, at least, two types of traps for deuterium in Be exposed to D atoms – one kind of traps with deuterium in the atomic state and the other with deuterium in the molecular state. For all experimental temperatures after 1 h exposure time, deuterium is mainly trapped in the atomic state. At 740 K the amount present as D atoms is $Q_D = 2.25 \times 10^{16}$ D/cm² and exceeds that in the form of D₂, $Q_{D_2} = 1 \times 10^{15}$ D/cm² by more than 20 times, i.e. $Q_D:Q_{D_2} \approx 20:1$. However, when the exposure time increases up to 4 h they become

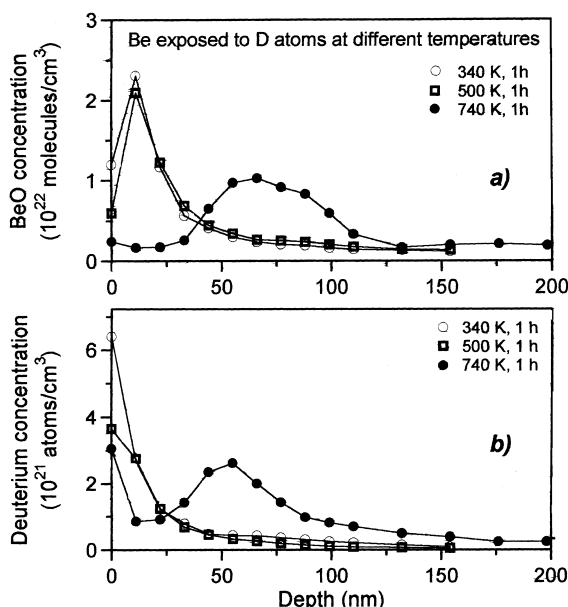


Fig. 1. Depth profiles of BeO (a) and deuterium (b) in Be samples exposed to D atoms for 1 h at 340, 500 and 740 K. Deuterium profiles represent the sum of D atom and D₂ molecule concentration distributions. The combined SIMS and RGA measurements were done within 22 h after D atom exposure.

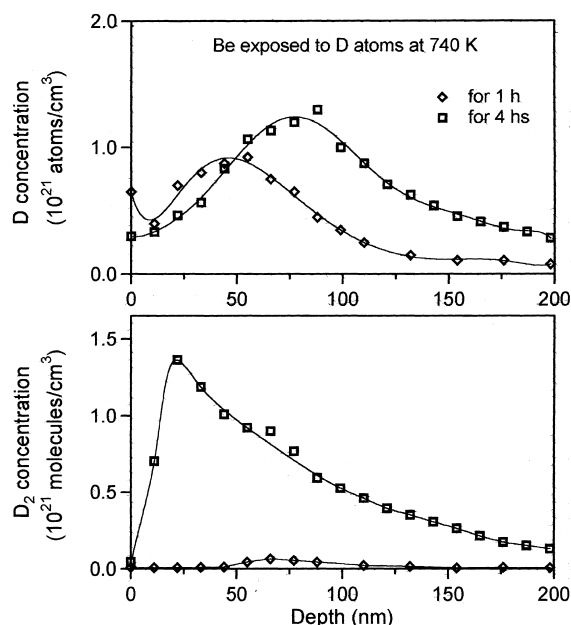


Fig. 2. Concentration profiles of deuterium trapped as D atoms (on the top) and as D₂ molecules (on the bottom) in a Be sample exposed to D atoms at 740 K for 1 and 4 h. The SIMS and RGA measurements were performed ~ 500 h after D atoms exposure.

approximately the same: $Q_D = 4.7 \times 10^{16}$ D/cm² and $Q_{D_2} = 4.2 \times 10^{16}$ D/cm². Thus, when the exposure time increases, the deuterium part in the molecular state grows faster (more than a factor of 30) than that in the atomic state (less than a factor of 2).

It was found that the deuterium content in beryllium oxide decreased if the samples were kept in vacuum or air at room temperature. This decrease (dependent on the storage time) is shown in Figs. 3–5 for the samples which were exposed to D atoms at different temperatures. It is seen that this decrease takes place mainly for the atomic part of the trapped deuterium. It decreased gradually over a long time (more than 500 h). For the molecular part, an initial drop was observed on the sample that was exposed at 740 K only. Probably, this drop is connected with carbon which appeared at the sample surface at this temperature. After this drop the molecular part of deuterium content did not change with time. The molecular parts of trapped deuterium in the samples which were exposed to D atoms at 340 and 500 K were, within experimental error, constant independent on the storage time.

The kinetic curve showing a decrease of atomic part of trapped deuterium with storage time is given in Fig. 6 for the sample exposed at 340 K. This curve was obtained using the data of Fig. 3. Similar curves were calculated for other temperatures of D atom exposure. Kinetics of deuterium release proved to be the same independent on the temperature of sample loading by

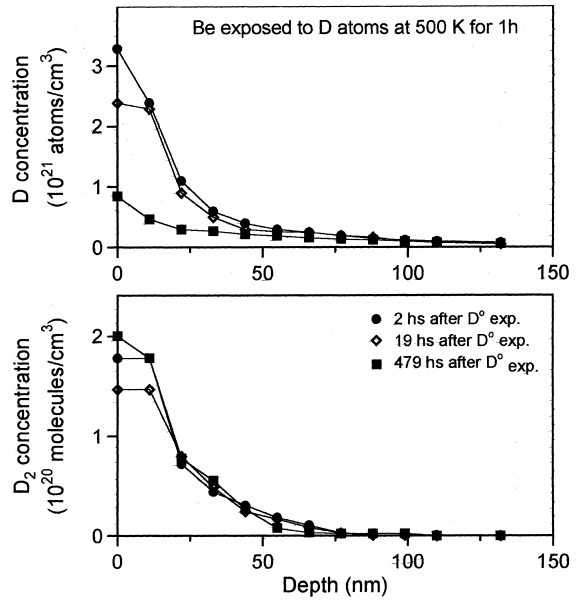


Fig. 4. Evolution of D atom concentration (on the top) and D₂ molecule concentration (on the bottom) in a Be sample exposed to D atoms for 1 h at 500 K, as a function of storage time in vacuum at room temperature.

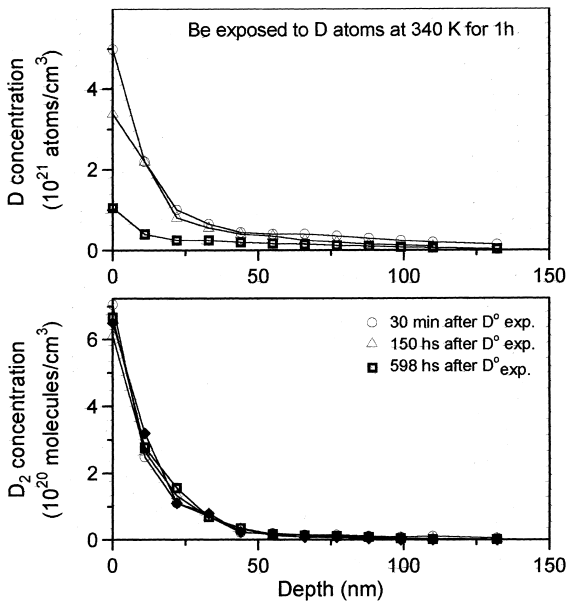


Fig. 3. Evolution of D atom concentration (on the top) and D₂ molecule concentration (on the bottom) in a Be sample exposed to D atoms for 1 h at 340 K, as a function of storage time in vacuum at room temperature.

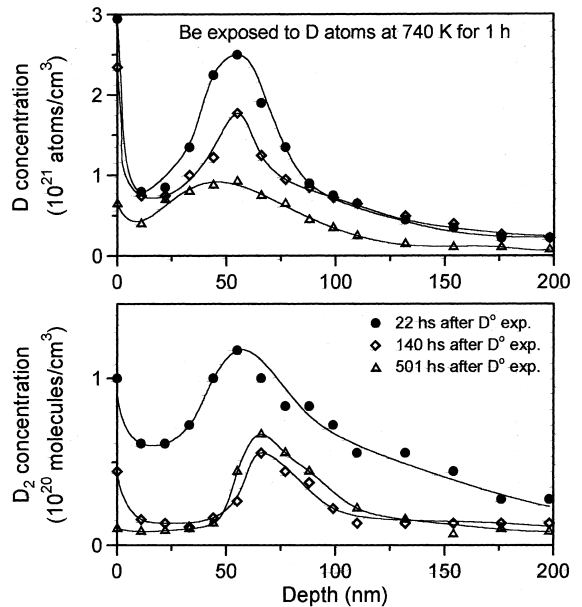


Fig. 5. Evolution of D atom concentration (on the top) and D₂ molecule concentration (on the bottom) in a Be sample exposed to D atoms for 1 h at 740 K, as a function of storage time in vacuum at room temperature.

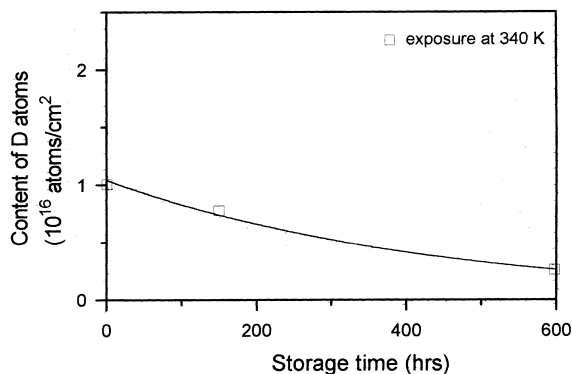
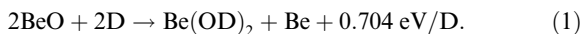


Fig. 6. Kinetics of decreasing of atomic deuterium content as a function of storage time. The sample was exposed to D atoms at 340 K.

atomic deuterium. The calculated kinetic constant is equal to $k = (1-3) \times 10^{-5} \text{ min}^{-1}$.

The decrease of amount of implanted deuterium in Be with storage time was also observed in Ref. [4]. It was reported that during the 14 h after the end of an irradiation by 5 keV D_2^+ -ions, the deuterium content in Be decreased approximately by a factor of 1.5. The effect was explained by deuterium thermal diffusion at room temperature.

It was suggested in our previous work [1] that under D atom exposure deuterium trapping in beryllium oxide occurs as a result of chemical reactions with hydroxide formation [5].



The presence of a BeOD^- line in SIMS spectra confirms the formation of hydroxylic OD^- groups. The atomic part of trapped deuterium may be explained by deuterium retention in the hydroxide. This suggestion is also confirmed by the fact of oxide layer growth on the sample side which was exposed to atomic deuterium [1]. Really, according to reaction (1), the formation of the hydroxide is accompanied by the release of free beryllium atoms. These beryllium atoms then react with residual oxygen forming the growing oxide layer.

These processes take place not only on the surface but in the beryllium oxide bulk as well. That means that deuterium atoms diffuse into the sample bulk and that free beryllium atoms (formed in the bulk) migrate to surface. Thus, deuterium accumulation in beryllium oxide is determined by deuterium diffusion, and oxide film growth – by beryllium atoms diffusion through the film. It was shown in Ref. [1] that under D atom exposure the increasing of amount of retained deuterium atoms N_D with the exposure time t_{exp} occurs as $N_D \sim \sqrt{t_{\text{exp}}}$ what really points out the diffusion character of the deuterium accumulation process. These data

gave the possibility of evaluating the effective diffusivity at 740 K; a value in the range 10^{-14} – $10^{-15} \text{ cm}^2/\text{s}$ was deduced, close to the deuterium diffusivity in beryllium oxide, $5 \times 10^{-15} \text{ cm}^2/\text{s}$ at the same temperature, reported by Fowler et al. [6].

Thus, the atomic part of retained deuterium is a result of the chemical reactions which occur in the beryllium oxide layer with hydroxide formation. The beryllium hydroxide formed is not stable and decays according to the reaction.



In Ref. [7] the experiments on the isothermal hydroxide decay at temperatures 528, 545, 561 and 578 K were described. The kinetic rate constants of hydroxide decay $k \text{ min}^{-1}$ and activation energy of this process, 14.7 kcal/mol, were obtained. Using these data we calculated the kinetic constant of hydroxide decay for room temperature which was proved to be equal to $\sim 10^{-6} \text{ min}^{-1}$. This value is about one order of magnitude less than that was obtained in our experiments $k = (1-3) \times 10^{-5} \text{ min}^{-1}$. Taking into account that the extrapolation to room temperature was carried out using only four points in a narrow temperature interval (50°), the error could be quite large and it is possible to say that both values are comparable.

Thus, we propose that the decrease of retained deuterium content during Be sample storage in air at room temperature is the process of deuterium release as a result of hydroxide decay.

Apparently, the molecular part of retained deuterium is connected with trapping of deuterium atoms in bubbles where they form molecules. Molecular deuterium filled bubbles were also observed in Be after irradiation by 9 keV D^+ -ions at 700 K [2,8]. Their appearance in the ion stopping zone was explained by the generation of radiation vacancies which together with thermal vacancies contribute to bubble nucleation and growth. As no defect generation occurs under exposure to D atoms, the probable explanation of the molecular fraction appearance in this case may be either (i) the high concentration of deposited D atoms giving conditions when bubble formation becomes energetically favorable and/or (ii) the formation of bubbles nucleating at oxide structure imperfections. The beryllium oxide layer grows under D atom exposure so that growth defects could be the initial centres where deuterium atoms combine into molecules.

4. Conclusions

Results obtained show that under D atom exposure deuterium is mainly accumulated in the beryllium oxide layer although long deuterium tails in bulk are observed as well. The atomic part of retained deuterium is

connected with deuterium trapping as a result of chemical reactions with hydroxide formation. It leads not only to deuterium accumulation but also to oxide film growth. The hydroxide formed is not stable and decays gradually during sample storage in vacuum or in air. Therefore the atomic part of retained deuterium decreases in time. The molecular part of retained deuterium is connected with trapping of deuterium atoms at structural defects of oxide layer where they form molecules what leads to bubbles growth.

Thus, although the common features of deuterium accumulation in Be under ion (or plasma) irradiation and under D atom exposure are similar, more detailed analysis reveals the differences. Thermal deuterium atoms penetrate into very short distance from the surface and are mainly retained in the oxide layer in atomic form in result of chemical reactions. On the contrary, the energetic ions penetrate deeply into the beryllium bulk and most of the deuterium in this case is retained in molecular form in bubbles and cavities in beryllium matrix within the ion stopping zone.

Acknowledgements

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