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Some peculiarities in the behavior of Be surfaces under bombardment by ions from a deuterium plasma

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Abstract

In experiments with Be mirrors bombarded by keV ions from a deuterium plasma a sharp drop of reflectance in the wavelength 220–650 nm was observed after quite low ion fluence although no mass loss of Be sample was measurable. Therefore such change of reflectance was ascribed to the transformation of the oxide layer, that naturally coats the Be mirror, into a hydroxide film. Supporting this hypothesis, the vacuum annealing of exposed samples at elevated temperature resulted in partial restoration of the reflectance. The effect of deuterium ion bombardment was closely related to the ion energy: the higher energy the deeper the drop of reflectance. In the paper we present results on the reflectance of Be mirrors depending on the experimental conditions, i.e., on the ion energy, annealing temperature, duration of exposure to bombardment by deuterium ions.

Keywords: Beryllium; Reflectance; Oxide; Hydroxide; Annealing

1. Introduction

During the last decade the interest grew on beryllium as a prospect plasma facing material in an experimental fusion reactor ITER [1]. Many papers were devoted to different aspects of Be interaction with H isotopes, however, the effects of such interaction on the optical properties of beryllium were not investigated till recently. Meanwhile, it was discovered in [2] that the modification of the optical properties of beryllium under hydrogen impact is very significant, allowing the study of some peculiarities of H–Be interaction.

In this paper we give the detailed description of results obtained in simulation experiments aiming to get data on the behavior of samples of Be mirrors subjected to bombardment by ions from a deuterium (D) plasma.

2. Experiment

As a plasma source a cw electron cyclotron resonance discharge at a frequency of 2.37 GHz was used, sustained inside a stainless steel vacuum chamber placed into a double-mirror type magnetic field. The vacuum vessel was evacuated by a turbomolecular pump down to a pressure ~1 × 10^{-4} Pa. During the discharge D_2 was

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fed continuously to maintain the pressure at a level of (3–5) × 10^{-2} Pa. Typical plasma parameters at injected 200–400 W UHF power were as follows: $n_e \leqslant 10^{10}$ cm^{-3} and $T_e \sim 5$ eV.

Using a copper holder the polished mirror samples, fabricated as plates with a maximal diameter of 22 mm, were inserted one by one into the plasma stream flowing out of the magnetic trap along the magnetic axis. The water-cooled holder was kept under a fixed negative voltage in the range of 0.05–1.35 keV. The ion current density onto the sample was close to 1 mA/cm^2.

The reflectance R of the samples for normal incidence in the wavelength region $\lambda = 220$–650 nm was measured ex situ after every exposure of the sample to ion bombardment (the accuracy of reflectance measurement was of the order 1%). The optical properties of the surface film were controlled by ellipsometry, and the surface micromorphology was observed by means of scanning electron microscopy (SEM). In parallel with measurements of R the samples were weighed within an accuracy of ~20 μg to control the ion erosion.

3. Results

The typical time dependences, $R(t)$, of Be mirrors are presented in Fig. 1 as measured for different wavelengths during erosion due to bombardment by D ions accelerated to the mirror surface by biasing the holder to $V = -1.35$ kV. The data of figure show that there are two very different parts of $R(t)$ behavior: an initial sharp drop of reflectance and a much slower gradual decrease with increasing the total exposure time. The sharp drop (by 5–8% in Fig. 1, depending on λ of reflected light) occurs after a few minute (2–5) exposures i.e., much before any mass loss becomes to be measured, the latter requires significantly longer exposure time (not less than 20 min). The absolute value of the sharp drop for different Be samples strongly depends on the pre-history of the sample as will be discussed below.

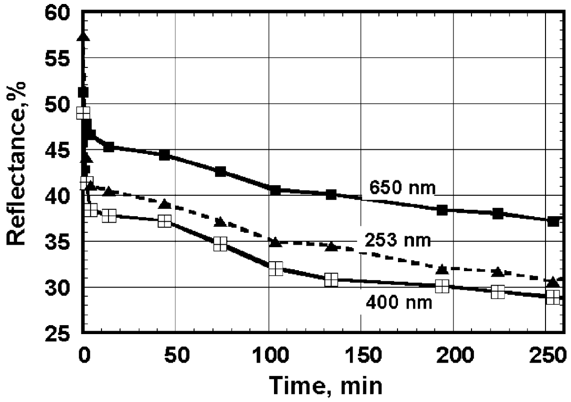

Fig. 1. Modification of Be mirror reflectance at the indicated wavelengths versus time of exposure to 1.35 keV ions of deuterium plasma at room temperature.

For the second part of $R(t)$ dependences of Fig. 1 the approximate proportionality of the mass loss to the total exposure time is characteristic. Therefore the slow decay of reflectance with increasing the time of ion exposure is probably a result of the increase of the mirror surface roughness due to ion erosion. Such $R(t)$ dependences were observed when the polycrystal mirrors of different metals have been extensively bombarded by D plasma ions, and the increase of the mean roughness of mirror surface was supported by SEM photos [3].

More interesting is the ‘mysterious’ sharp drop of Be mirror reflectance without any sputter erosion. Because of no mass loss, this reflectance drop has to be exclusively as the surface effect which proceeds due to impact of D ions. The most probable surface process is the transformation of the BeO film, covering the Be sample, into a Be(OD)$_2$ film according to reaction [4]

$$2\mathrm{BeO} + 2\mathrm{D} \rightarrow \mathrm{Be(OD)_2} + \mathrm{Be} + 0.7\ \mathrm{eV/D}. \tag{1}$$

The beryllium hydroxide film is known to disintegrate slowly at room temperature [4], but this process can be accelerated with increasing temperature [5]. In our experiments the annealing of exposed Be samples in vacuum at ~300 °C during ~2 h almost fully cancels the effect of $R(t)$ drop, i.e. after the annealing process the Be mirror reflectance is restored significantly, sometimes almost up to the initial magnitude.

From the fact that the observed effects of reflectance modification are connected with transformation of composition of a thin surface film, the optical properties of both film varieties have to be very different. A BeO film, which is an intrinsic component of Be surface, has a negligible absorptivity index value [6]. In contrast, the sharp drop of reflectance after exposure to ~1 keV ions is an indication that the absorptivity of the modified film is significantly different. The estimations of optical properties of the film after exposure of the Be mirror to D ions was made by using the results of ellipsometry measurement and gave the refraction coefficient $n \sim 2$ and the extinction coefficient $k \sim 0.1$, compare to values for the BeO film: $n \sim 1, 7$ and $k \sim 0$ [6].

The extent of the sharp drop of Be mirror reflectance rises with increasing D ion energy. As an example, Fig. 2 shows the variation of the mirror relative reflectance ($\Delta R = (R_E - R_0)/R_0$, where R_0 is the reflectance before ion exposure and R_E the reflectance after bombardment by ions with energy E) for five samples exposed to ions of different energy. The time of every exposure was 2 min, except for the time for the 50 eV ion energy (15 min). It is seen that after bombardment by 50 eV ions an increase of R was observed revealing the effect of surface cleaning. For the samples exposed to 100 eV ions a small

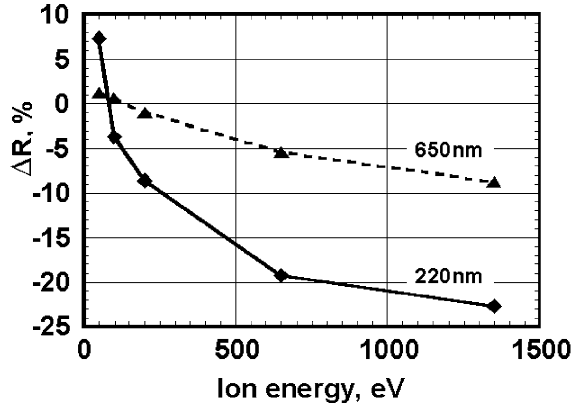

Fig. 2. Ion energy dependence of reflectance decrement of Be mirrors exposed to deuterium ions up to fluence $\sim 10^{18}$ D/cm^2.

degradation was registered only for the UV spectral range. However, the decrement ΔR in the sharp drop (characterizing the rate of mirror degradation) highly increased for a further rise of ion energy with evident tendency to saturate. Such a behavior of reflectance of Be samples with rising energy of D^+ ions can be qualitatively explained by a difference in the thickness of the transformed layer at different ion energy. The low energy ions (100 eV) have a short mean range in the BeO film and therefore only a thin outer layer of the BeO film is transformed into the hydroxide film. With increasing ion energy the thickness of hydroxide layer rises due to the increase of the mean range of ions inside the oxygen film and thus the portion of transformed oxide layer also grows. (Note, this model suggests that the BeO film has to be thicker than the mean range of D^+ ions with the highest energy used in experiment.) From calculations, the mean range of deuterium ions in the BeO environment increases according to relation: ρ_E (nm) $= 10.3E$ (keV). Thus, from data of Fig. 2, the energy of ions when the initial reflectance drop trends to saturate (after 2-min exposure) can be evaluated in the limit 1.5–2.0 keV. The saturation can be interpreted as the complete transformation of the BeO film into the hydroxide film. The comparison of Fig. 2 data with mean range dependence gives the approximate thickness of the oxygen containing layer in the interval ~15–20 nm. This value of Be oxide film looks quite reasonable.

The improvement of reflectance when Be mirrors was exposed to low energy ions, seen in Fig. 2, is very surprising. We checked that this is not a casual result by investigating the behavior of Be mirrors in several consecutive cycles: (1) short exposure to high-energy ions (1.35 keV), (2) annealing for ~2 h at different temperatures, (3) exposures to low energy ions (70 eV). Consequences of such tests for reflectance at two wavelengths are presented in Fig. 3. It is seen that every exposure to high energy ions is accompanied by a drop

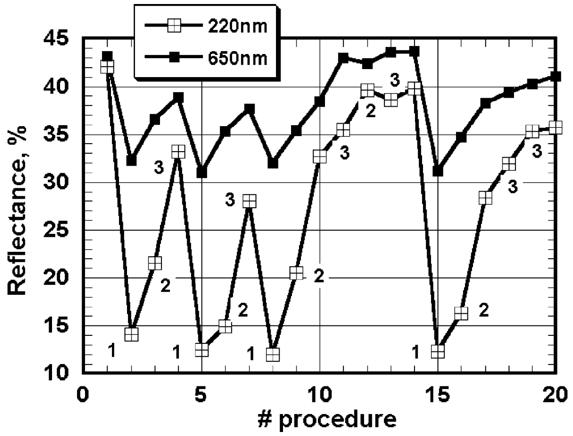

Fig. 3. Modification of Be mirror range under: (1) bombardment by 1.35 keV energy ions of deuterium plasma, (2) annealing for 2 h at different temperatures (100–200 °C), (3) bombardment by 70 eV energy ions of deuterium plasma.

of reflectance, especially deep for shorter wavelength. The annealing of the sample or the exposure to low energy ions gives rise to some restoration of reflectance, but restoration of R is stronger for low energy ion bombardment.

4. Discussion

It was suggested in the previous section that the sharp drop of reflectance of Be mirror after rather small fluence of D^+ ions ($\sim 10^{18}$ ions/cm^2) is due to transformation of BeO film into a hydroxide film according to reaction (1). In addition to such transformation, the appearance of other Be compounds (e.g., carbides and hydrides) inside the BeO layer or underneath also cannot be excluded. However, following [7] the reactions with formation of Be_2C occur at temperatures >500 °C, i.e. much above the temperature typical for our experiments. At the same time, the BeH^+ and BeD^+ ions were registered very distinctly [8] together with fragments of $Be(OD)_2$ molecules when a Be sample was bombarded by mixture $Ar^+ + D^+$ ions during measurement of the SIMS-mass-spectra without any heating of sample.

A direct proof of realization of reaction (1) would be, probably, the registration of heavy water (D_2O) during annealing of the Be sample preliminary exposed to D^+ ions flux, because the process of $Be(OD)_2$ disintegration follows the reaction: $Be(OD)_2 \rightarrow BeO + D_2O$. Up to now we did not find any publication where D_2O peak would be controlled directly among the products released from Be samples during thermal desorption after bombardment by deuterium ions.

In the case the process (1) predominates over others, it will result in a gradual increase of the thickness of an oxide or hydroxide layer on the surface of the Be sample subjected to D ions or atoms if the partial pressure of oxygen-containing molecules is high enough. The oxygen accumulation will be due to the appearance of free Be atoms displaced because of reaction (1) directly inside the BeO + $Be(OD)_2$ film. Besides, development of a void structure in this film and in the near surface region of the beryllium body is highly probable under long-term bombardment by D atoms (or ions) [10], revealing an increase of the probability for displaced Be atoms to combine with oxide to form BeO molecules. The growth of the thickness of oxygen-containing film on Be surface under D ion bombardment was observed in [9,10]. Without heating the growth of such films would be highly probable in ITER FEAT where Be protection of the wall is planned [1], if the partial density of oxygen-containing molecules will be not negligibly low (e.g., close to that of experiments [9,10] or to conditions in our ECH discharge). This is because the flux of D and T atoms to Be surface calculated in [11] for this device, $\sim 2 \times 10^{15}$ atom/cm^2 s, is factor ~5 below the flux of D ions in the present experiments. Therefore, the time needed for the oxygen-containing film to be fully sputtered would be, correspondingly, several times longer than the value found in our simulation experiments (>20 min) and by far exceeding the pulse duration in ITER FEAT (~8 min).

However, at sufficiently elevated wall temperature in ITER FEAT (~300 °C), both reactions – formation and disintegration of Be hydroxide – would go simultaneously, thus the process (1) may not be taken into account.

It should be noted that the saturation of the sharp drop of Be mirror reflectance with increasing D^+ ion energy (Fig. 2) does not mean that at this stage of the experiment the BeO was fully transformed into a $Be(OD)_2$ film. This follows, in particular, from result obtained in [12,13] when the ratio of implanted D atoms to BeO molecules was found to be ~0.25 and ~0.2, correspondingly for implantation of 5 keV D^+ and 3 keV D^+ ions into BeO film at room temperature. For the full transformation this ratio should be equal to unity in accordance with formula (1).

5. Conclusion

1. A strong effect on reflectance in UV and visible parts of spectrum was found for Be mirrors subjected to bombardment by ions of deuterium plasma. The effect depends on the energy of D^+ ions and is probably connected with different mean ranges of D^+ ions inside the BeO layer that coats the Be mirror.
2. The effects of reflectivity change is suggested to be due to partial transformation of the top BeO layer into a $Be(OD)_2$ film.
3. The annealing in vacuum of Be mirrors exposed to D^+ ion bombardment reveals in the partial restoration of the Be mirror reflectance due to disintegration of the $Be(OD)_2$ film. Similar to the annealing effect significant restoration of reflectance was observed after additional exposure to low energy D^+ ions.
4. The effect of the reflectance modification of Be mirrors is very strong (more than 20% absolute in the UV region), thus it can be used for an *in situ* investigation of interaction of beryllium with hydrogen isotopes.

Acknowledgements

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