ELSEVIER

Journal of Nuclear Materials 283–287 (2000) 1094–1099

journal of nuclear materials

www.elsevier.nl/locate/jnucmat

Codeposition of deuterium ions with beryllium oxide at elevated temperatures

A.V. Markin [a], V.P. Dubkov [a], A.E. Gorodetsky [a], M.A. Negodaev [b], N.V. Rozhanskii [a], F. Scaffidi-Argentina [c,*], H. Werle [c], C.H. Wu [d], R.Kh. Zalavutdinov [a], A.P. Zakharov [a]

[a] *Institute of Physical Chemistry, Russian Academy of Sciences, Leninsky pr. 31, 117915 Moscow, Russian Federation*
[b] *Lebedev Physical Institute, Russian Academy of Sciences, Leninsky pr. 53, 117924 Moscow, Russian Federation*
[c] *Forschungszentrum Karlsruhe-IKET, Inst. f. Neutronenphysik and Reaktort., Postfach 3640, 76021 Karlsruhe, Germany*
[d] *EFDA-CSU, Boltzmannstrasse 2, 85748 Garching, Germany*

Abstract

Deuterium-loaded BeO films were produced by sputtering the beryllium target with 10 keV Ne ions in D_2 gas at a pressure of approximately 1 Pa. The sputtered beryllium reacts – on the substrate surface – with the residual oxygen, thus forming a beryllium oxide layer. Biasing the substrate negatively with respect to the target provides the simultaneous bombardment of the growing film surface with D ions formed by Ne–D_2 collisions. Substrate potential governs the maximum energy of ions striking the growing film surface while its size governs the flux density. According to X-ray photoelectron spectroscopy (XPS), electron probe microanalysis (EPMA) and reflection high energy electron diffraction (RHEED) data, the beryllium is deposited in the form of polycrystalline hcp-BeO layers with negligible (about 1 at.%) carbon and neon retention. Thermal desorption spectroscopy (TDS) data shows a strong deuterium bonding, with a desorption peak at 950 K, in the films deposited at −50 and −400 V substrate potentials. In addition, a relatively high ratio $D/BeO \approx 0.2$ has been found in the BeO films even at a substrate temperature of 800 K. Microstructural features of mixed Be–C–O films are presented as well.

1. Introduction

The codeposition of energetic hydrogen isotope ions with plasma facing component (PFC) materials could constitute an important safety issue for the next step fusion reactors [1]. Materials eroded from the PFC will be redeposited, during normal operating conditions of the reactor, in different areas of the tokamak vacuum chamber (e.g., cooler areas of the divertor). Depending on the quantity of material eroded and the amount of tritium retained in the redeposited material, the integral tritium inventory in the reactor could be significantly increased.

Codeposition of tritium with carbon was extensively studied in the past and the mechanisms are well understood. However, other materials (e.g., beryllium and tungsten) are under consideration as candidate PFC materials for a next step fusion reactor. Therefore, the modifications of the codeposited film properties during the reactor operation as well as the H-retention behavior are of great interest. Beryllium has a very strong affinity for oxygen, therefore a certain amount of BeO will be always present in the codeposited films.

In the present work, the deuterium retention in growing BeO layers has been investigated using a conventional ion sputtered technique modified for deposition of hydrogen loaded films. Microstructure features of the mixed Be–C–O films are presented as well.

2. Experimental

A schematic drawing of the deposition technique is shown in Fig. 1. The sputter target and the substrate are

---

[*] Corresponding author. Tel.: +49-7247 822 047; fax: +49-7247 824 837.

E-mail address: francesco.scaffidi@iket.fzk.de (F. Scaffidi-Argentina).

0022-3115/00/$ - see front matter © 2000 Elsevier Science B.V. All rights reserved.
PII: S0022-3115(00)00286-5

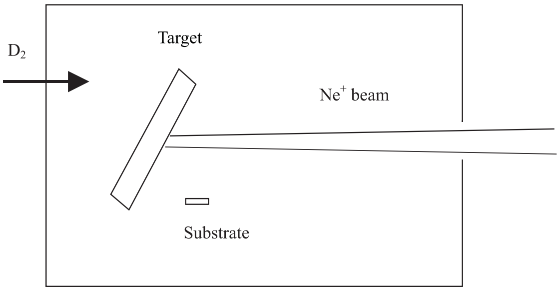

Fig. 1. Basic scheme of the deposition technique.

placed in a separated chamber installed into a high vacuum accelerator facility with background pressure of 10^{-4} Pa. A beam of 10 keV neon ions passes through a 6 mm diaphragm on the target titled at 45° to the beam axis. Sputtered atoms are deposited at the substrate located at a distance of 2 cm perpendicular to the sputter spot. For production of deuterium-loaded films, molecular deuterium is admitted in the chamber to a pressure of about 1 Pa. Biasing the substrate negatively with respect to the target provides the simultaneous bombardment of the growing film surface with deuterium ions extracted from deuterium plasma generated by Ne^+–D_2 collisions. The incident deuterium flux seems to contain both D^+ and D_2^+ ions forming directly by Ne^+–D_2 collisions with a portion of D_3^+ ions resulting from their drift in molecular deuterium. Sputtered particles leaving the target surface in the form of positive ions can also be collected at the biased substrate and therefore make a contribution to the film growth. The maximum energy of all positive ions incident on the growing film surface is governed by the substrate potential. In addition, the film is bombarded with backscattered neon particles.

Small $3 \times 3 \times 0.05$ mm^3 tungsten substrates were used. They were forced against a nickel strip of 0.3 mm thickness by two nickel plates spot-welded to the strip itself. The strip was heated ohmically. The substrate was slightly bent to provide a better thermal contact with the heated strip.

The areal densities of oxygen, carbon and neon retained in the films were determined by quantitative electron probe microanalysis (EPMA) method making corrections for oxygen and carbon present in the bulk of substrate [2]. Chemical composition and chemical bonding characteristics were analyzed by X-ray photoelectron spectroscopy (XPS) using Al anode radiation.

After slight sputter cleaning in the XPS apparatus, the tungsten substrates with codeposited films were cut into small pieces of about 1×1 mm^2 in size for thermal desorption spectroscopy (TDS) analysis. Thermal desorption measurements were carried out in an ultra high vacuum (UHV) chamber with a background pressure of 10^{-6} Pa. The specimens were clamped between two nickel strips heated by an electric current. The sample temperature was measured by W–Re thermocouples spot-welded to one of the strips. The release of D_2 and HD molecules was monitored by a quadrupole mass-spectrometer (QMS). The QMS was calibrated against calibrated H_2 and D_2 leaks. The sensitivity to HD was assumed to be the average of the H_2 and D_2 sensitivities.

The film microstructure was analyzed by reflection high energy electron diffraction (RHEED) method at an accelerating voltage of 50 kV and by transmission electron microscopy (TEM). For TEM, films deposited on NaCl substrates were used. The NaCl substrate was scratched from a face covered by the deposit into small pieces (3×3 mm^2), and afterwards a film was detached from this substrate by slowly immersing it into the hot water. All the specimens were investigated in TEM EM 400T operated at 100 kV.

3. Results and discussion

3.1. Codeposition of deuterium with BeO

For deposition of BeO films a hot-pressed beryllium target was used. The target was sputtered at a neon ions current of 0.8 ± 0.1 mA for 30 min. Sputtered beryllium reacted on the tungsten substrate with residual oxygen to form beryllium oxide layers. Three codeposited films were studied in this work. Deposition conditions are presented in Table 1.

According to the RHEED data, the films are polycrystalline hcp-BeO with crystallite size ranging from 2 to 20 nm. EPMA measurements show negligible (about 1 at.%) carbon and neon retention. The Be 1s photoelectron spectrum consists of a single peak at a binding energy of 114 eV suggesting that the deposited beryllium is totally oxidized [3]. This allows us to make an estimation of the beryllium deposition rate and the film thickness from oxygen areal density assuming the formation of stochiometric hcp-BeO.

Deuterium ion flux was evaluated by measuring the difference in electric current flowing to the substrate in the course of vacuum and D_2 atmosphere sputtering. No special experiments were performed to measure the composition and the spatial distribution of the incident deuterium ions over the substrate. Therefore the mean deuterium flux density was estimated by measuring the total current flowing to the substrate and assuming that only the D_2 ions bombard the substrate. The results of calculations are collected in Table 1.

The film thickness for 400 eV bias is approximately twice that for a 50 V bias. There seem to be at least two reasons for this effect. First, by varying the deuterium pressure the D ion flux was set to be the same for all the deposition runs. As the deuterium ion flux increases with

Table 1
Deposition conditions and composition of the D–BeO codeposited films

Substrate temperature (K)	Substrate bias (V)	BeO film thickness (nm)	Beryllium deposition rate (10^{18} Be m^{-2} s)	Deuterium flux density (10^{18} D m^{-2} s)	D/BeO ratio
600	400	110	4.5	5	0.17
800	50	53	2.1	5	0.04
	400	87	3.5	5	0.19

substrate potential, D_2 pressure for 50 V run was higher than that for 400 V, namely 0.8 and 0.3 Pa, respectively. It could lead to more intensive scattering of sputtered beryllium atoms in the 50 V run compared to 400 V run. Furthermore, it is known that the ionization coefficient of beryllium sputtered particles might be as high as 6% [4]. Assuming the cosinoidal angle distribution for the sputtered atoms, about 1% of the sputtered beryllium is estimated to be deposited at the substrate. Therefore the bias dependence of film thickness could be explained by different efficiency of Be ion collection for different substrate biases.

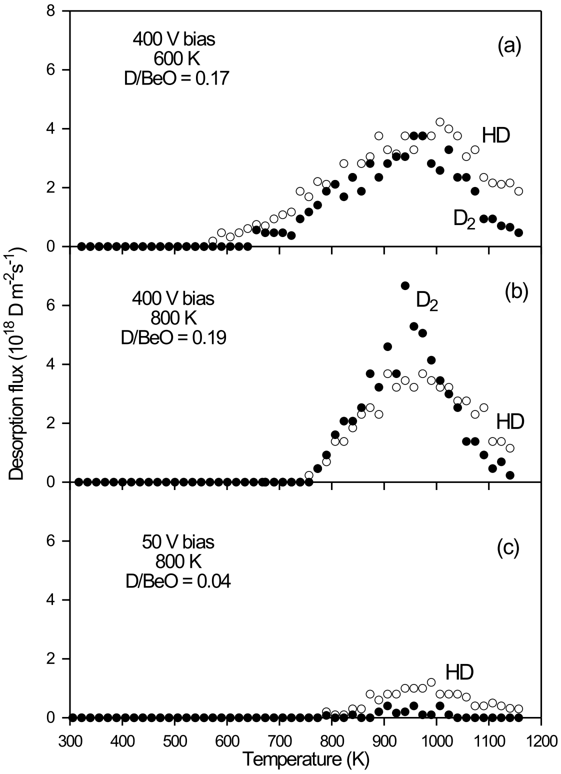

Fig. 2. Thermal desorption fluxes of the D_2 and HD molecules from BeO films deposited on tungsten substrates held at a bias of 400 V and temperatures of 600 K (a), 800 K (b), and at a bias of 50 V and a temperature of 800 K (c). Heating rate: 1 K s^{-1}.

Release spectra of D_2 and HD molecules from the codeposited films grown on the substrates biased to 400 V are shown in Figs. 2(a) and (b). It should be noticed that this bias leads to the bombardment of the growing film surface by D ions with a maximum energy of 400 eV. The spectra consist of a single peak centered at 950 K. Integrating the spectra gives approximately the same deuterium areal density of 1.3 ± 0.2 D m^{-2} for the 600 and 800 K films which corresponds to a mean deuterium concentration D/BeO = 0.2.

The spectra for 50 V bias are shown in Fig. 2(c). In this case, the energy of D ions is not in excess of 50 eV. TDS shows a similar desorption behavior as for the 400 V bias but both desorption flux and total retained deuterium is a factor of five smaller. The corresponding D/BeO ratio is evaluated to be as low as 0.04.

The data on D–BeO codeposition obtained in the present work as well as the results from [5,6] are summarized in Fig. 3. In both the works cited earlier, the codeposited films were produced using in principle the same technique. The beryllium target is irradiated with 1.5 keV D ions [5] or with 100 eV D ions [6]. Sputtered beryllium reacts at the substrate with residual oxygen to form beryllium oxide layers, whereas the growing film surface is bombarded simultaneously with backscattered deuterium particles. Flux ratios and particles energies evaluated in the papers from TRIM calculations are shown in Table 2.

As was shown the deuterium concentration for high energy ion sputtering [5] is higher than that for low energy ion sputtering [6]. The difference in deuterium concentrations is most pronounced at substrate temperatures above 600 K. It should be noted that the use of more energetic primary deuterium ions leads to higher energy of backscattered deuterium. In addition, it gives rise to the long tails in energy distribution of sputtered beryllium particles whereas the main part of them has energy of several eV [5].

Therefore, it is reasonable to suggest that the deuterium energy plays a crucial role in the codeposition. The experimental points at 800 K shown in Fig. 3 confirm this result. Of special interest is the different D/BeO ratio measured at 800 K for 400 V bias in the present work and at 770 K by Mayer [5]. A possible reason for this discrepancy might be due to a significant flux of 400 eV secondary Be$^+$ ions striking the growing film surface in our experiments. Considering the peak position of the

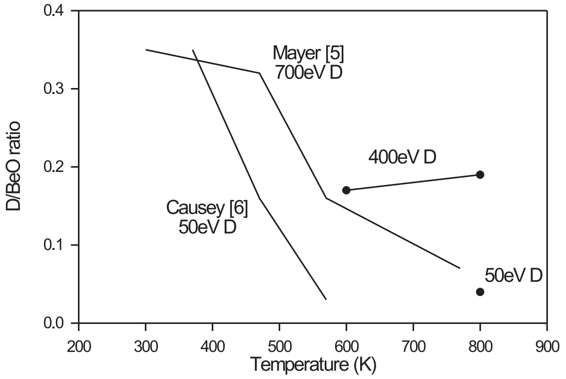

Fig. 3. D/BeO ratio as a function of the test temperature with indicated the maximum energy of the deuterium particles incident at the growing film surface.

TDS spectra shown in Fig. 2, a significant decrease in deuterium retention is expected only above 1000 K.

For the International Thermonuclear Experimental Reactor (ITER) reference edge plasma ('semi-detached' regime using ~1% neon to radiate heat), the plasma temperatures along the divertor targets vary from about $T_i \sim T_e \sim 1$ to 30 eV. Considering the sheath potential, redeposited beryllium ions (average charge state ~2) impact the surface at about $10 \times T_e$ or about 10–300 eV [7]. The energies in the redeposition dominated areas are at the lower end of this range, or roughly <100 eV [7], but far exceed a mean sputtered particles energy typical in a few eV. This factor should be properly assessed

Table 2
Fluxes ratios and particles energies in the codeposition experiments

Refs.	Beryllium (eV)	Deuterium/ tritium (eV)	D, T/Be flux ratio
Mayer [5]	1–10	0–700	~1
Causey et al. [6]	1–10	0–50	≫1
Present work	(1–10) and 50	0–50	2.5
	(1–10) and 400	0–400	1.5
ITER [7]	20–100	10–50	≫1

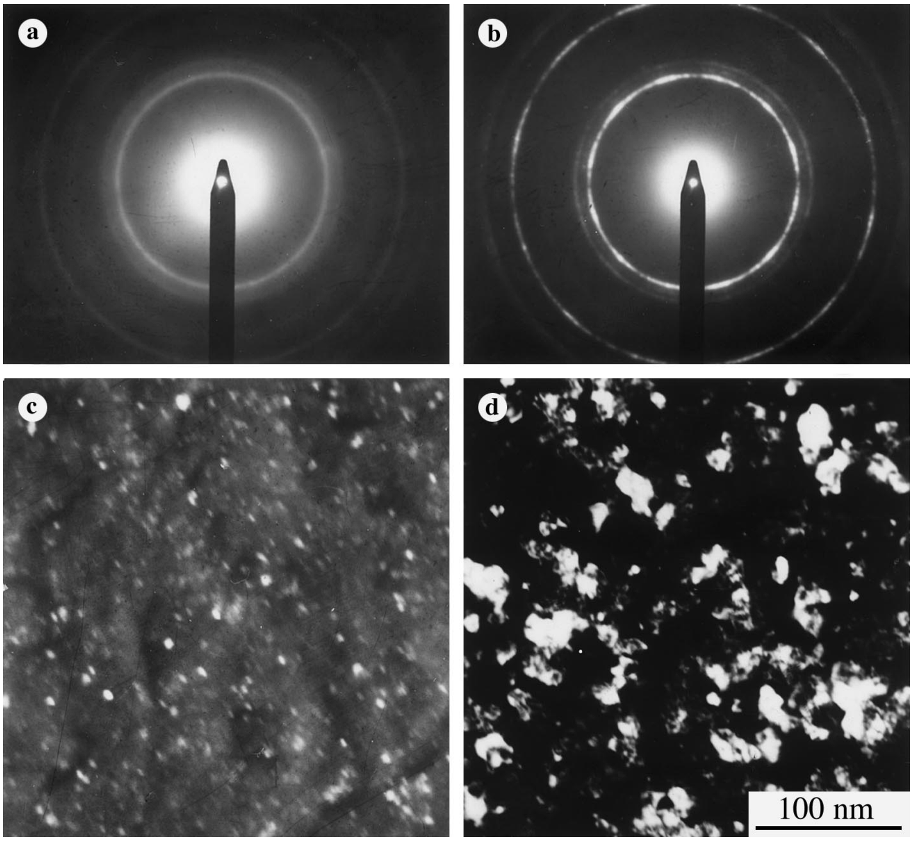

Fig. 4. Diffraction patterns (a, b), and DF images (c, d) of the mixed Be–C–O and BeO film deposited at 600 K in a vacuum of 10^{-4} Pa.

when considering the results of laboratory experiments on hydrogen codeposition.

3.2. Microstructure of ion sputtered BeO and BeO + C films

The characteristics of deposition of beryllium oxide films with carbon were investigated. For this investigation, a mixed Be/C target was sputtered with 10 keV ions in a vacuum of 10^{-4} Pa. The films were deposited on a 0.3 mm thin highly polished Si single crystal plates and on NaCl single crystal substrates held at temperature of 600 K. According to EPMA measurements, the films grown on both substrates contain approximately the same amount of carbon and oxygen. In addition, pure BeO films were deposited under the same conditions using the Be target.

The films deposited on NaCl substrate were studied by means of TEM. Comparison between diffraction patterns of the films (Figs. 4(a) and (b)) shows that the mixed film contains a significant amount of fine-crystallite hcp-BeO phase. An appearance of the halo around the central spot (Fig. 4(a)) seems to be explained by the presence of amorphous carbon. The arrow shows an additional ring for interplanar spacing of 0.151 nm, which might be related to the most intensive line (2 2 0) of Be_2C having interplanar spacing of 0.153 nm. However, we failed to detect the order lines of Be_2C. From DF images of the films (Figs. 4(c) and (d)), it follows that an addition of carbon leads to the formation of smaller BeO crystallites.

The films deposited in the same runs on Si substrates were studied by XPS. The Be 1s and C 1s spectra are shown in Fig. 5. The Be 1s spectrum consists of a single line at a binding energy of 114 eV suggesting that the mixed beryllium/carbon film is totally oxidized. No evidence of carbide formation is present as is shown in C 1s spectrum (Fig. 5). The peak at 284 eV is related to C 1s spectrum of carbon whereas the presence of Be_2C would lead to an additional peak at 282 eV [8]. The nature of the additional line in the diffraction pattern is not yet understood.

The simultaneous deposition of ion sputtered beryllium and carbon atoms (the main part of which have energy of several eV) on a substrate held at a temperature of 600 K in a vacuum of 10^{-4} Pa leads to the growth of beryllium oxide crystallites embedded in an amorphous carbon matrix. This result agrees with the annealing behavior of a Be–C system in oxygen atmosphere. In fact, by using the XPS technique, Nieh et al. [8] found carbide bonds in the mixed Be–C layer during the annealing of beryllium specimens which were covered with a 200 nm carbon film at temperatures above 700 K. As the sample heating was performed in a relatively poor vacuum of about 10^{-4} Pa, the beryllium in the mixed Be–C layer was fully oxidized from the outer surface to a depth of about 30 nm due to the higher thermodynamic stability of BeO in comparison with Be_2C. Thus, tritium and BeO codeposition seems to contribute in additive manner to the total tritium retention in the Be–C mixed material. However, a question arises whether the beryllium oxide is formed in a similar way in the films grown under conditions where more energetic beryllium and carbon particles are in present in the incident flux (i.e., similar to the conditions expected at the ITER divertor vertical target).

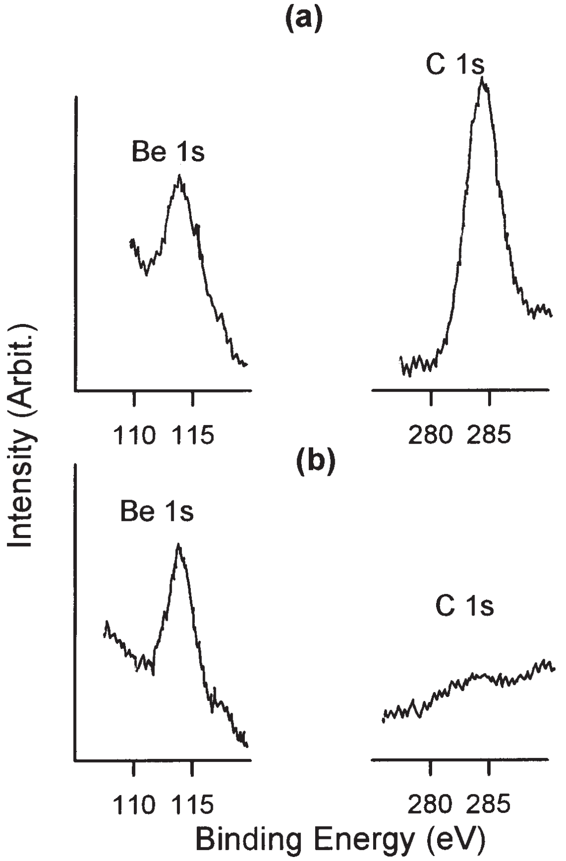

Fig. 5. Be 1s and C 1s photoelectron spectra of the mixed Be–C–O (a), and the BeO (b) films deposited at 600 K in a vacuum of 10^{-4} Pa.

4. Conclusions

A relatively high D/BeO ratio of about 0.2 has been found in the D–BeO codeposited films even at substrate temperature of 800 K. Considering the peak position of the corresponding TDS spectra, a significant decrease in deuterium retention is expected only above 1000 K.

Simultaneous deposition of ion sputtered beryllium and carbon atoms on a substrate held at a temperature of 600 K in a vacuum of 10^{-4} Pa leads to the growth of beryllium oxide crystallites embedded in a amorphous carbon matrix. This leads to the tentative conclusion that tritium and BeO codeposition will contribute in additive manner to total tritium retention in the codeposited Be–C–O mixed films.

There are good reasons to believe that BeO crystallites formed in the Be–C–O mixed deposit will be stable under air/oxygen heating to about 700 K. If the air heat treatment will be selected for the tritium removal from the in-vessel surfaces, then the BeO dust containing up to 20 at.% hydrogen isotopes might be formed after the carbon of the mixed codeposit has been completely eroded.

References

[1] G. Federici et al., in: Proceedings of the ISFNT-4, Tokyo, Japan, 6–11 April 1997.
[2] V.Kh. Alimov et al., J. Nucl. Mater. 196–198 (1992) 670.
[3] C.D. Wagner et al., Handbook of X-ray Photoelectron Spectroscopy, Perkin Elmer, Eden Prairie, 1979.
[4] H.E. Beske, Z. Naturforsch. A 22 (H.4) (1967) 459.
[5] M. Mayer, J. Nucl. Mater. 240 (1997) 164.
[6] J.N. Brooks et al., J. Nucl. Mater. 241–243 (1997) 294.
[7] J.N. Brooks, September 1998, private communication.
[8] T.G. Nieh et al., Scr. Metall. 20 (1986) 87.