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Sputtering of beryllium, tungsten, tungsten oxide and mixed W–C layers by deuterium ions in the near-threshold energy range

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Abstract

An experimental method of determination of sputtering yield for current-conducting materials under ion bombardment of light gases in the near-threshold energy range has been developed. Such an information is very important in both the purely scientific and applied aspects. This method is based on the use of special regimes of field ion microscopic analysis. The procedure of measuring the sputtering yield includes cleaning of the surface in situ by desorption and evaporation of atoms by the field in order to make atomic-clean and atomic-smooth surface. This method permits to observe single vacancies in the irradiated surface, i.e., directly to count the single sputtered atoms. It has been used for beryllium, technically pure tungsten, tungsten oxide and mixed W–C layer on the tungsten irradiated by deuterium ions. The energy dependence of sputtering yield of those materials by deuterium ions at energies ranging from 10 to 500 eV is investigated. Experimental results for beryllium are in a satisfactory agreement with the calculations of Eckstein et al. Substantial connection between threshold energy of the sputtering and condition of oxidized surface of tungsten has been ascertained. The threshold energy for sputtering of oxidized tungsten surface is equal to 65 eV. The threshold energy for sputtering of mixed W–C layer has almost the same value as for the pure W. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Beryllium; Carbon deposition; Low energy deuterium incidence; Sputtering yield

1. Introduction

Beryllium, carbon–carbon composites and tungsten are considered at present as candidate-materials for International Thermonuclear Experimental Reactor (ITER). The presence of various materials, as the divertor and the first wall components, will unavoidably result in the formation of mixed layers on the surfaces of plasma facing components.

Tungsten is characterized by a high mass number and by a high self-sputtering yield, but also by a high threshold energy for sputtering [1]. However, as a result of the great chemical affinity of tungsten to oxygen its surface is oxidized. As shown in experiments, presence of the oxide film on the surface of tungsten produced under a high partial pressure of residual oxygen (8×10^{-5} Torr) in the vacuum chamber causes a considerable (approximately by a factor of 10) reduction in the threshold energy for sputtering of W bombarded with light ions, as a result of reduction in the binding energy of tungsten oxide molecules [1]. But in contrast to tungsten the threshold energy for sputtering of BeO is higher than that of pure beryllium. Under conditions of redeposited materials of an ITER divertor, the surface of tungsten will be covered with a mixed W–C layer. Determination of the sputtering threshold energy of tungsten covered with the mixed W–C and oxide layers is of the principal importance.

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It should be noted that the experimental determination of the sputtering threshold energy requires the implementation of extremely sensitive high resolution techniques allowing in situ cleaning of the surface and directly to observe each vacancy produced by the bombarding ions on the surface, i.e., to take each atom removed from surface into account. Among modern experimental means of surface diagnostics, the technique of field ion microscopy was used to study the surface structure of atomic layers, production, behaviour and evolution of defects in a crystalline structure, as has been shown in Refs. [2,3] this technique responds to such requirements for current-conducting materials.

In this present work the technique of field ion microscopy was first used for determining the threshold energy for sputtering of pure beryllium and tungsten, tungsten oxide and mixed W–C layers on the tungsten surface, bombarded with deuterium ions, as well as the energy dependence of the sputtering yields by deuterium ions in the near-threshold energy range.

2. Experimental technique

The field ion microscope is based on the processes taking place in electric fields with a strength of 10^8–10^{10} V/m. The main element of the field ion microscope is a needle-like sample (cathode) and the anode as a fluorescent screen. One can realize the processes of evaporation and desorption in strong electric fields, along with an autoionization. In such cases, the surface atoms are removed at any temperatures. The phenomenon of desorption is similar, in principle, to that of evaporation by the field. The differences between the evaporating fields and the desorbing ones are related to a different nature of the bond among the particles removed from the surface.

Field ion microscopic analysis of samples is being completely optimized and standardized [4] for the study of tungsten and tungsten-based composite materials. In the present work an attempt was made for the first time to fulfill the same task for beryllium. The extreme difficulty of beryllium samples investigation in a field ion microscope arises from a relatively low melting point (∼1290°C) of beryllium and the rather low binding energy of beryllium atoms, respectively. Following the original technique described in Ref. [5], the evaporative field value for beryllium was found to be $F_e \sim 28$ V/nm. This value is much below the electric field strength value required for helium autoionization (helium is the most appropriate gas for obtaining images in field ion microscope; since for its ionization a field strength of $F_i \sim 44$ V/nm is required). Due to the fact that for beryllium $F_e \leqslant F_i$, microscopic images of beryllium in helium are unstable, though providing atomic resolution in a number of areas.

To overcome the above difficulty, a technique for obtaining and analysis of desorption images (that is, images in vacuum in the own ions [6]) was realized in the present work. The appearance of single vacancies on the surfaces of irradiated beryllium samples was registered, primarily, by the high-accuracy measurements of the variation in the images general brightness (measurements of the value of desorption current were taken from a micro-channel plate [7] placed in front of the fluorescent screen of the microscope), and only rarely by direct visual observation.

The sputtering yield of tungsten and its compounds was determined by direct count of the number of formed vacancies (see, for example, the field-ion image of the surface of a pure tungsten sample in Fig. 1: single vacancies formed during a single irradiation pulse are marked with arrows).

The experiments were performed in the field ion microscope [8]. For samples irradiation the technique of pulsed two-step reversal of high strength polarity was developed and applied. Ionization of the gas, serving simultaneously an image-forming purpose, occurred by the mechanism of electron impact at the moment a short high-voltage pulse of reverse (negative) polarity was fed, and the generation of autoelectrons by the sample took place. The duration of such 'ion-generating' high-voltage pulses did not exceed 0.1 μs, at amplitude of 5 kV. Together with the high-voltage pulse, a low-voltage negative pulse was applied to the sample with pulse duration being $\geqslant 10$ μs, while the amplitude corresponding to the preset energy of bombarding ions varied from 10 to 500 V with step of 10 V. Concurrently various check analyses were conducted, which realized various sequences of pulses and their parameters.

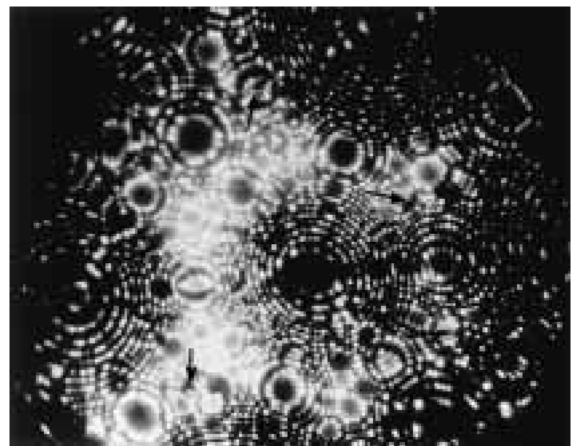

Fig. 1. The field-ion image of the surface of a pure W sample: single vacancies formed during a single irradiation pulse by D^+ ions are marked with arrows.

Implementation of cleaning the surface from the adsorbed particles and formed films in the process of measuring the sputtering yield in situ allows to carry out the sputtering measurements from an atomic-pure surface.

The procedure of measuring of the sputtering yield includes the following operations.

(a) Manufacture of pointed samples and their installation in the field ion microscope capable of ensuring three duties of operation: as a proper field ion microscope, as a desorption ion microscope, and as a field-emission microscope [3].

(b) Evacuation of the microscope with subsequent deuterium filling; initially vacuum of 3×10^{-9} Torr was reached, after deuterium filling the pressure was between 10^{-6} and 10^{-5} Torr.

(c) Preliminary field-ion and (or) desorption microscopic analysis of an initial surface, its cleaning by evaporation in the field in order to make the atomic-clean and atomic-smooth surface.

(d) Ionization of the deuterium gas which serve in the same time as imaging gases.

(e) Surface irradiation by D^+ ions, providing the pulsed alternation of the voltage polarity at the sample; the energy of bombarding ions is controlled by a change in the amplitude and duration of a direct pulse.

(f) Repeated field-ion and (or) desorption microscopic analysis of the irradiated sample surface in order to identify single vacancies in it, i.e., direct count of the sputtered atoms.

(g) Evaluation of sputtering yields corresponding to the given energy of bombarding ions.

For the same sample the operations (c)–(g) were repeated many times. The number of 'irradiating' voltage pulses was varied from 10 to a few hundred in the cases of low values of the sputtering yields.

An important step in the process of sputtering yield evaluation was the determination of irradiation fluences. In the present work, the irradiation fluence was computed from the formulas derived by the authors in Ref. [9] (see also Ref. [2]). The required values for average work function φ for Be, W, WO and WC (3.92, 4.54, 5.0 and 3.6 eV, respectively) were taken from Ref. [10]. At the specified irradiation parameters the surface point with the tip average radius $R_o \sim 100$ nm was exposed to $\sim 2.5 \times 10^7$ impacts of D^+ ions per second, or 250 ions per pulse, which corresponds to a flux density of 2.5×10^{17} ions/cm^2 s. That means for a sputtering yield $Y \approx 10^{-1}$ about 25 single vacancies are observed on the entire sample surface viewed through the microscope after one irradiating pulse (the field-ion image of the pointed sample tip surface with $R_o \sim 100$ nm shows $\geqslant 10^5$ atoms) and equivalent for $Y \approx 10^{-3}$ only 1 vacancy over 4 pulses.

The needle-point samples of Be were produced by electrochemical etching in concentrated H_3PO_4 at 30–50 V dc. In the case of tungsten, electrochemical etching went in 1.5 N solution of NaOH at 5–10 V dc.

For producing an oxide layer on the surface of tungsten the samples were heated under the atmosphere up to the temperature of $\sim$750°C. The films of a W–C mixture were produced by collection of the products of simultaneous tungsten and graphite sputtering by 20 keV Ar^+ ions on the needle-like and massive samples.

The thicknesses of oxidized and mixed layers, their roughness and a chemical composition were determined with the profilemeter made by Sloan Instruments and by the Auger electron srectroscopy (AES), in combination with the layer-after-layer etching from masssive samples. Phase composition of the targets was investigated using X-ray analysis of crystalline structure in the sliding beam geometry.

3. Results and discussion

3.1. Threshold energy for sputtering

In Table 1 the experimental results of sputtering threshold energies by deuterium and helium ions for the pure Be W, mixed W–C layer and for tungsten oxide are compared with those of the published experimental and theoretical data [1,11].

From Table 1 it follows that the values, E_{th}, measured by the new method for pure beryllium bombarded with D^+ and He^+ ions are in satisfactory agreement with experiments performed for Be irradiated with D^+ and He^+ ions at 923 K in JET tokamak and also with the calculations of Eckstein et al. [11]. The literature value of the sputtering threshold energy for Be at the room temperature during irradiation is considerably higher. The reason for this high value is probably surface oxidation of the beryllium which leads to higher threshold energy for sputtering due to the higher surface binding energy of oxides.

No significant differences are observed between the values of E_{th} for W and mixed W–C layer bombarded with D^+ ions. The results for W and W–C layer are in a good agreement with an earlier measurement of threshold energy for sputtering of W and W–C by D^+ ions [11–15].

The threshold energy for sputtering of tungsten oxide by deuterium ions measured by field ion microscopic technique is 65 eV, in contrast to the $E_{th} \cong 18$ eV in Ref. [1], where tungsten oxide is produced during irradiation with D^+ ions under background oxygen pressure of 8×10^{-5} Torr and the yield is measured by the weight loss method. A low E_{th} is obtained due to an assumed low surface binding energy ($E_B = 0.3$ eV) of the tungsten oxide molecules [1]. In our experiments on the surface of tungsten a stable oxide film, $\sim$50 nm thick is

Table 1
The measured threshold energies for sputtering compared to literature values

No.	Material	Ion	T(K)	E_{th} (eV) experimental	E_{th} (eV) experimental [1,11–14]	E_{th} (eV) theoretical
1	Be	D^+	78–373	<10		
			923		10 [11,14]	9,8 [11]
			293		26,2 [11]	
2	Be	He^+	293	<10	44,5 [11]	30 [12]
			923		13,9 [11,14]	13,9 [11,14]
3	W	D^+	293	160	175 [12]; 178 [11]	201 [11]; 160 [13]
4	W+C	D^+	78–293	150		
5	WC	D^+			171 [11]; 150 [12]	
6	Tungsten oxide	D^+	293	65	<18 [1]	

produced. An estimate of the surface binding energy from Ref. [1] gives its value of ∼1.1 eV.

The drastic increasing of sputtering threshold energy by D^+ ions for tungsten oxide layer observed by means of the new technique may also be attributed to the differences of sputtered particles composition between these two methods. The new method identifies only W-vacancies, i.e., counts only the W sputtered atoms, the weight loss method registrates all sputtered surface atoms, including adsorbed atoms and molecules.

3.2. Energy dependence of sputtering yield for beryllium by D^+ and He^+ ions

Fig. 2 shows the measured sputtering yields of beryllium bombarded with deuterium and helium ions at energies from 10 to 200 eV (points). The energy dependences of Be sputtering yields with D^+ and He^+ ions calculated by Eckstein et al. [11] and averaged experimental data for combinations Be–D^+ and Be–He^+ [15,16] are also given in this graph. The agreement between experimental sputtering yields of beryllium measured by the field ion microscopic technique and computer simulation data [1] is quite good. While the averaged experimental data from Refs. [15,16] in near-threshold energy range have lower values in comparison with calculated curves due to the presence of oxide film on the beryllium surface.

One should note that the production of vacancies in the energy range under study was observed in the first surface layer only. As a result, in the energy range 10–200 eV, the sputtering of beryllium atoms takes place from the first monolayer on the surface.

3.3. Energy dependence of sputtering yield for W, WO, W–C by deuterium ions

The Auger electron analysis of the mixed W–C layer shows that in the layer, ∼10^4 nm thick, W and C are distributed uniformly and the oxygen impurity on the surface does not exceed 9.5 at.%. As a result of tungsten heating in air, the WO-layer thickness on tungsten is ∼50 nm.

The energy dependence of sputtering yields for tungsten by deuterium ions is given in Fig. 3 (curve 1). In Fig. 3 in addition to our experimental results, also experimental (curve 2) and calculated (curve 3) energy dependence of sputtering yield for combination W–D^+ is presented. The sputtering yields of tungsten, measured by various techniques are rather close to each other, being in a sufficiently good agreement with a theoretical curve.

The energy dependence of the sputtering yields for the redeposited W–C layers and WC [11] also practically coincides (Fig. 4).

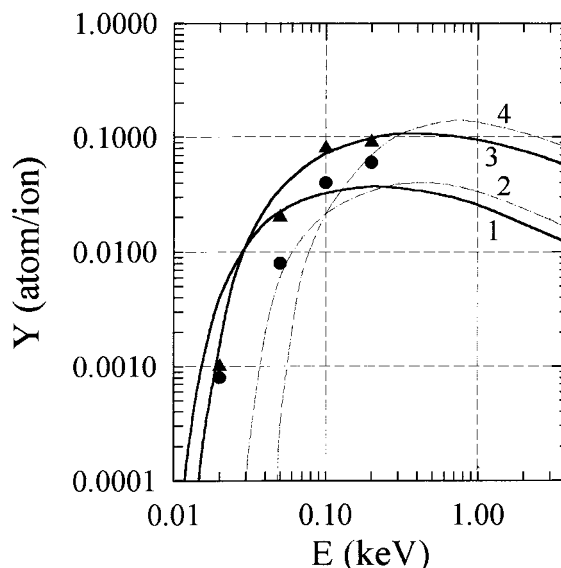

Fig. 2. Energy dependence of sputtering yield of Be with D^+ and He^+ ions at room temperature: (●) this work, Be–D^+; (▲) this work, Be–He^+; (1) calculated data for Be–D^+ [11]; (2) averaged experimental data for Be–D^+ [11]; (3) calculated data for Be–He^+ [11]; (4) averaged experimental data for Be–D^+ [11].

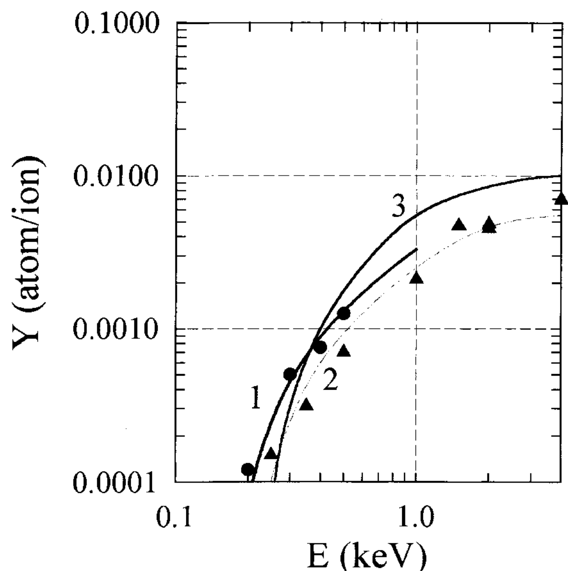

Fig. 3. Energy dependence of the sputtering yield of tungsten bombarded with deuterium ions: (1) this work, experimental data (●) for W–D^+; (2) experimental data (▲) for W–D^+ [11]; (3) calculated data for W–D^+ [11].

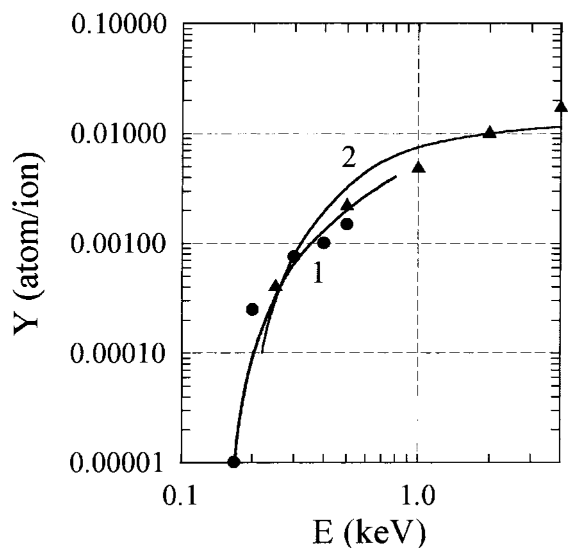

Fig. 4. Energy dependence of the sputtering yield of mixed W–C layer on tungsten (1) and WC (2) [11,13] bombarded with deuterium ions: (●) this work, experimental data for mixed W–C layer; (▲) experimental data for WC [11,13].

An energy dependence of the sputtering yield of tungsten oxide by deuterium ions (curve 1) is given in Fig. 5. For comparison, on the same graph, the experimental data by Roth et al. [1] for the tungsten sputtered by D^+ ions under oxygen pressure of 8×10^{-5} Torr

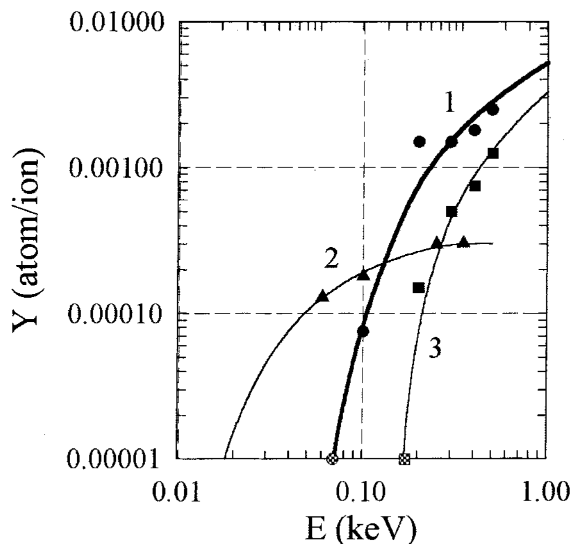

Fig. 5. Energy dependence of the sputtering yield of tungsten oxide (curve 1), (curve 2) – from [1] and tungsten (curve 3) [1] bombarded with deuterium ions: (●) this work, experimental data for tungsten oxide; (▲) experimental data for W–D^+ under oxygen pressure of 8×10^{-5} Torr [1]; (+) experimental data for W–D^+ [1].

(curve 2), as well as those for pure tungsten (curve 3), are given. In the energy range <100 eV, the sputtering yields for tungsten irradiated under high pressure of oxygen essentially exceed the corresponding sputtering yields measured by the field ion microscopic technique. At $E > 350$ eV the sputtering yield values for tungsten oxide measured by weight loss technique (curve 2) approach to the sputtering yields for W (curve 3). It means that, when the sputtering yield rises up to 3×10^{-4} at./ion under experimental conditions [1], the oxide film on the tungsten surface has been sputtered by D^+ ions.

4. Conclusions

1. The advantages of the field ion microscopic technique are:
   - The possibility of cleaning the surface in situ from adsorbed atoms and molecules of residual gases, from oxygen film, etc.
   - The possibility to observe each vacancy produced by the bombarding ions upon the surface, i.e., count each sputtered atom.
2. The drastic increasing of the threshold energy for sputtering of tungsten oxide bombarded with deuterium ions is observed. The sputtering threshold, E_{th}, measured by new field ion microscopic technique is equal 65 eV.
3. The threshold energies for sputtering of pure beryllium irradiated with deuterium and helium ions at

room temperature are in satisfactory agreement with the calculations of Eckstein et al., but significantly lower than those values determined by the weight loss method at room temperature.

4. The energy dependences of sputtering yield for pure W and for mixed W–C layer on tungsten bombarded with D^+ ions correspond to the earlier published data for W and WC.
5. The production of vacancies in the energy range under study was only observed in the first surface layer.

Acknowledgements

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