Sputtering of tungsten, tungsten oxide, and tungsten–carbon mixed layers by deuterium ions in the threshold energy region

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An original experimental method is developed for determining the sputtering coefficients of electrically conducting materials during bombardment by light gas ions at threshold energies. This information is very valuable in both purely scientific and practical terms. The basis of the method is a special field-ion-microscopic analysis regime. The procedure for measuring the sputtering coefficients includes cleaning the surface by field desorption and evaporation, with the subsequent work on an atomically clean and atomically smooth surface. The method permits identification of single vacancies on the irradiated surface, i.e., it is possible to count individual sputtered atoms. The method is tested on commercially pure tungsten, tungsten oxide, and a W–C mixed layer on tungsten under deuterium ion bombardment. The energy dependences of the sputtering coefficients of these materials for sputtering by deuterium ions at energies of 10–500 eV are obtained and analyzed. An important relationship between the energy threshold for sputtering and the conditions for oxidation of tungsten is found. The energy threshold for sputtering of an oxidized tungsten surface is 65 eV. The energy threshold for sputtering of the W–C mixed layer is almost equal to the corresponding value for pure tungsten. © *1999 American Institute of Physics.* [S1063-7842(99)02909-8]

INTRODUCTION

Carbon composites (CFC) and tungsten are currently under examination as candidate materials for controlled thermonuclear reactor designs. CFC and tungsten are to be used for the most energy stressed parts of the diverter system, which are subjected to high fluxes of particles and electromagnetic radiation from the plasma. The presence of different materials in the components of the divertor and first wall will inevitably lead to the formation of pulverized, mixed layers on the surface of the facing materials in the divertor and first wall.

Tungsten is characterized by a high mass number and, because of this, a high self-sputtering coefficient. In addition, because of the high chemical affinity of tungsten for oxygen, its surface is always oxidized. It has been established[1] that the presence on a tungsten surface of tungsten oxide, formed during bombardment of the tungsten surface by light ions when a high partial pressure of oxygen is present (8×10^{-5} Torr) in a vacuum vessel, causes a substantial reduction in the threshold for sputtering of tungsten owing to a drop in the binding energy of the atoms to the surface.

Under conditions such that the materials in the divertor and first wall of a thermonuclear reactor are pulverized, the surface layer of tungsten will consist of a mixture of tungsten and oxygen atoms. In this regard, a study of the effect of oxide and mixed W–C layers on the threshold sputtering energy of tungsten is of fundamental importance.

It should be noted that the experimental determination of sputtering thresholds requires especially sensitive, high-resolution methods capable of observing each vacancy formed on a sputtered surface by a bombarding ion (i.e., of counting each atom removed from the surface). Of the modern experimental techniques for surface diagnostics, these requirements are best met by field-ion microscopy, which is widely used for examining the structure of surface atomic layers, studies of the formation, behavior, and evolution of defects in crystal structure, and analyzing various radiation defects on the surface and in the volume of electrically conducting materials.[2,3]

In this paper field-ion microscopy is used for the first time to determine the energy thresholds for sputtering of tungsten, tungsten oxide, and mixed W–C layers on tungsten by D^+ ions, as well as to measure the energy dependences of the sputtering coefficients of these materials for sputtering by D^+ ions in the threshold energy region.

EXPERIMENTAL TECHNIQUE

We have used standard needle tips for field-ion microscopy with average radii of curvature at the tip on the order of $\overline{R_0}\leqslant 100$ nm as test samples in this work. In order to obtain a layer of oxide on the tungsten surface, the samples were heated in the atmosphere to a temperature of $\sim 750\,^{\circ}$C. Films of a W–C mixture were prepared by collecting the products of simultaneous sputtering of tungsten and graphite by 20 keV Ar^+ ions on needle and bulk samples of tungsten. The area of the ion beam was 2×10^{-2} m^2. The collectors

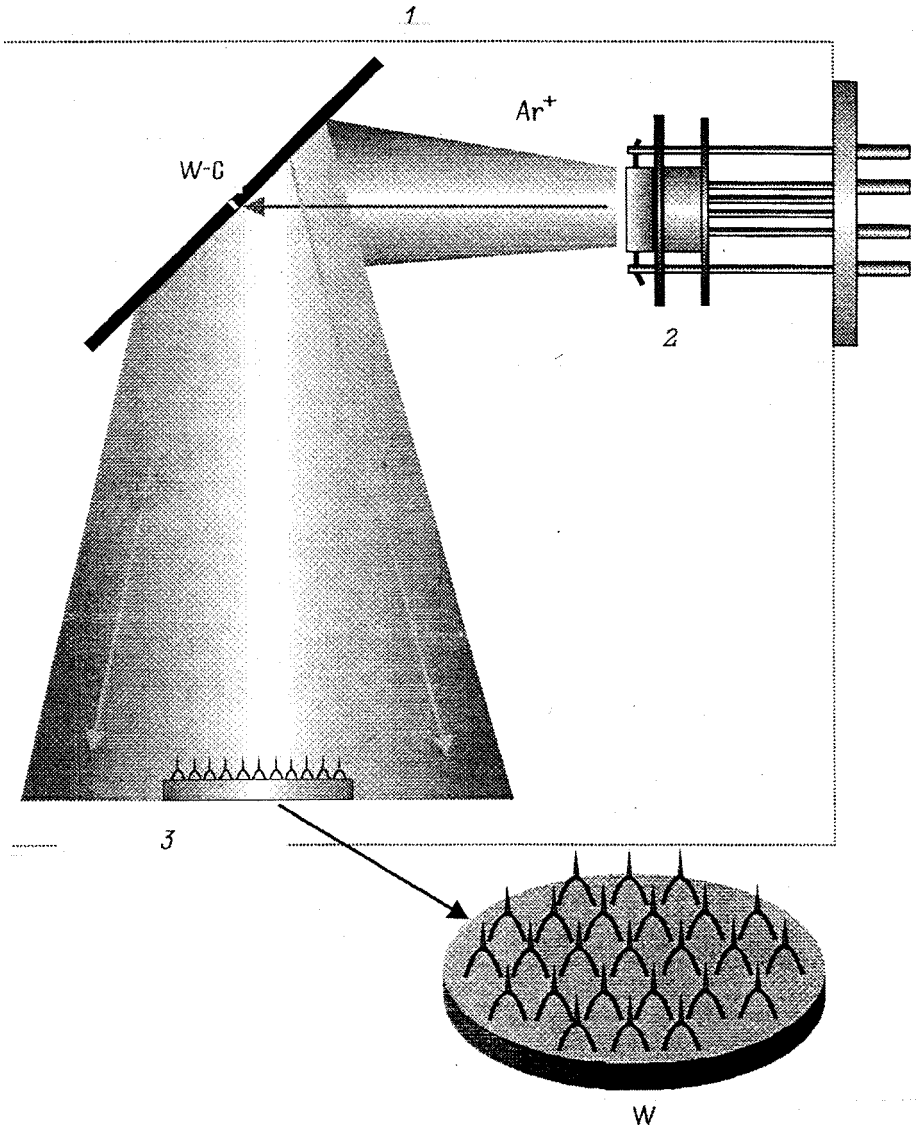

FIG. 1. Experimental apparatus for creating mixed W–C layers on the surface of tungsten samples– tips for field-ion-microscopy: *1* — vacuum chamber, *2* — ion source, *3* — collector.

were placed a distance of 25 mm from the sputtering targets. Figure 1 is a sketch of the apparatus used to deposit the mixed layer.

The thicknesses of the oxide and mixed layers, and their roughness and chemical composition were determined using a Sloan Instruments profilometer and Auger electron analysis in combination with layer-by-layer etching on the bulk samples. The phase composition of the samples was determined using x-ray structural analysis in a grazing incidence beam geometry. Figure 2 shows a typical depth distribution of oxygen on the oxidized tungsten surface, and Fig. 3 shows the depth distribution of carbon in a W–C mixed layer.

In this paper the sputtering coefficient of tungsten and its compounds was determined by directly counting the number of vacancies that were formed. (See, for example, the field-ion microscope image of a pure tungsten surface in Fig. 4, where the individual vacancies formed during a single beam pulse are indicated by arrows.)

A field-ion microscope of original design[4] at the Institute of Theoretical and Experimental Physics was used in our experiments. In order to form a system of pulses between the needle sample (cathode) and the microchannel plate (anode), a metal-ceramic cathode assembly grid was used. This assembly was placed in the spacce between the sample and fluorescent screen only during single beam irradiation pulses.

An original method for a pulsed two-step change in the polarity of the high voltage was developed and used for irradiating the samples. Here the gas, which could also serve for imaging, was ionized by electron impact at the moment a short high-voltage pulse of the opposite (negative) polarity was delivered and the sample generated electrons by field emission. These ''ion imaging'' high-voltage pulses were shorter than 0.1 μs and their amplitude was 5.0 kV. At the same time as the high-voltage pulse, a low-voltage negative pulse was applied to the sample; its duration was $\geqslant 10\,\mu$s and its amplitude, which was varied between 10 and 500 V with a step of at least 10 V, corresponded to the specified energy of the bombarding ions. Various control analyses were carried out in parallel, with a different sequence of pulses and their parameters (in diode and triode configurations; in the latter case the above mentioned cathode assembly grid was used).

The procedure for measuring the sputtering coefficients involved the following basic operations: a) fabrication of the

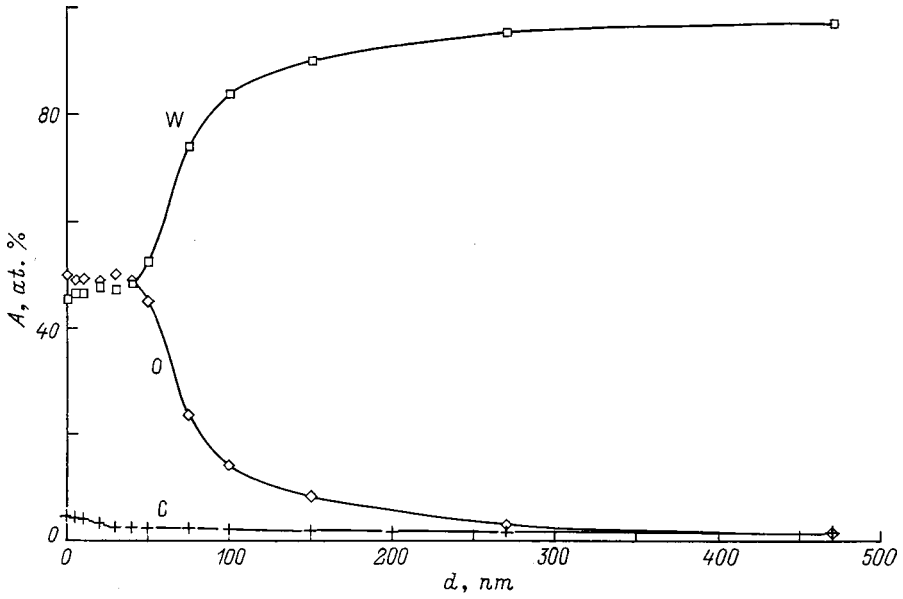

FIG. 2. Depth distributions of elements in the surface layer of WO after oxidation of tungsten samples: A is the concentration and d the depth.

sample tips and their installation in a field-ion microscope capable of operating in three modes: a field-ion microscope *per se*, a desorption ion microscope, and a field-emission microscope;[5] b) vacuum pumping of the microscope and admission of deuterium; the initial vacuum was 3×10^{-9} Torr, and the pressure after the deuterium was admitted was 10^{-6}–10^{-5} Torr; c) a preliminary field-ion or desorption microscopy analysis of the initial surface, cleaning and evaporation of the surface by the field to ensure maximum smoothness; d) pulsed irradiation of the sample surface by D^+ ions; e) a second microscopic analysis of the samples with the object of identifying the formation of isolated vacancies on their surface; and, f) calculation of the sputtering coefficients corresponding to the given bombarding ion energy. For a given sample, operations c–f were repeated many times. The number of bombarding pulses ranged from 10 to several hundred for low sputtering coefficients.

An important stage in the procedure for determining the sputtering coefficients Y was calculating the irradiation fluences. We emphasize that this is by no means a trivial problem. This problem, together with the estimate of the bombarding ion energy and the calculation of the number of individual vacancies formed during bombardment, imply a certain arbitrariness in the resulting values of Y. In this paper, the irradiation fluence was calculated using the formulas of Ref. 6. Here the required values of the average work function $\overline{\varphi}$ for W, WO, and WC (4.54, 5.0, and 3.6 eV, respectively) were taken from Ref. 7. For the given irradiation parameters, the surface of a tip with an average radius at its end of $\overline{R_0}$ $\approx$100 nm experienced $\sim2.5\times10^7$ D^+ ion impacts per sec-

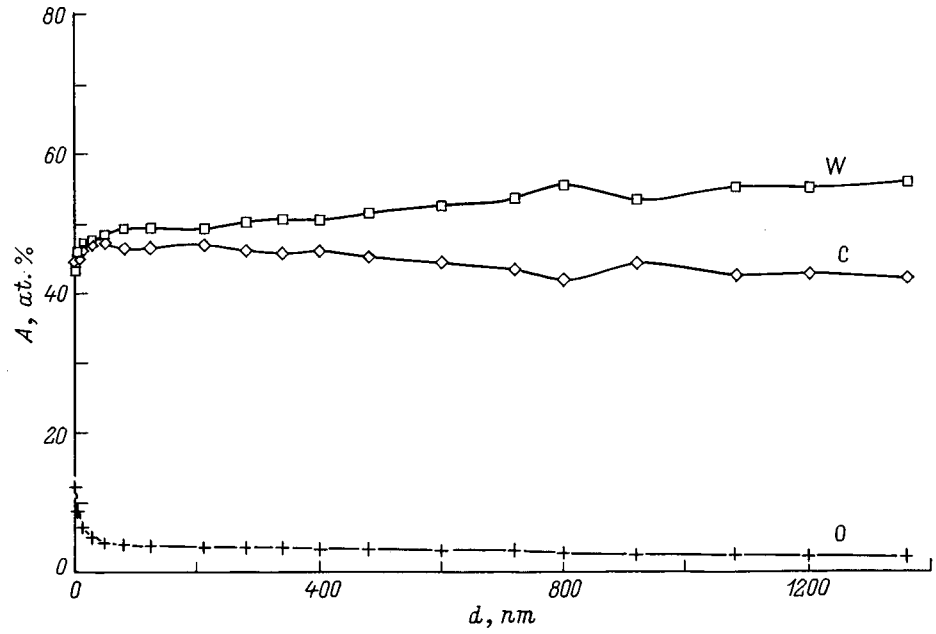

FIG. 3. Depth distribution of elements in a mixed surface layer of W–C on a tungsten sample.

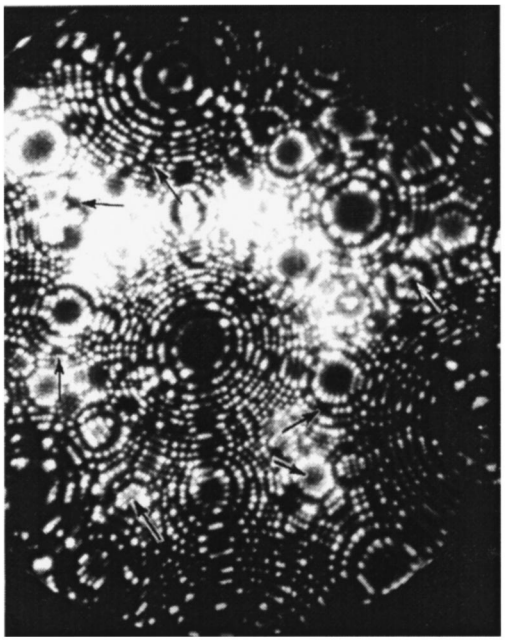

FIG. 4. Field-ion microscope image of the surface of a sample of pure tungsten: the arrows indicate individual vacancies formed as a result of a single pulse of D^+ ions.

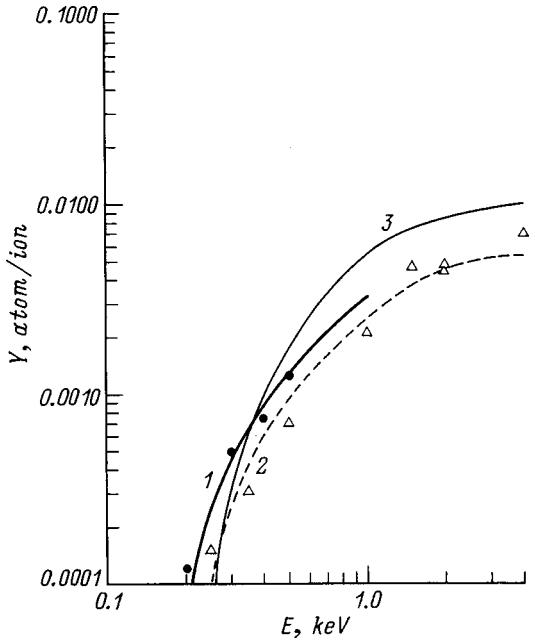

FIG. 5. Energy dependence of the sputtering coefficient Y of tungsten for sputtering by D^+ ions: *1* — results of the present work, *2* — experimental data of Ref. 9, *3* — theoretical calculation[9].

ond, which corresponds to 250 ions striking the sample surface during a single pulse or a flux of 2.5×10^{17} ions/cm^{2}s. In turn, $Y\approx10^{-1}$ corresponds to the observation of 25 individual vacancies over the entire sample surface observed under the microscope after a single beam pulse (the field-ion image of the end surface of a sample tip with $\overline{R}_0\sim100$ nm contains $\geqslant10^5$ atoms), $Y\approx10^{-2}$ corresponds to an observation of 5 vacancies in two beam pulses, $Y\approx10^{-3}$ corresponds to observation of 1 vacancy in 4 pulses, etc.

EXPERIMENTAL RESULTS

Table I is a comparison of the experimental values of the threshold sputtering energies of pure tungsten, tungsten carbide, a mixture of W–C, and tungsten oxide by deuterium ions, together with corresponding published experimental and theoretical data.[1,8–10]

The table shows that during D^+ ion bombardment there are no significant differences between E_{thr} for W and for a W–C mixed layer. The results for W and the W–C mixture are in good agreement with previous measurements of the threshold sputtering energy of W and W–C.[1,8,9]

TABLE I. Threshold sputtering energies.

Material No.	Material	T, K	E_{thr}, eV (experiment, present paper)	E_{thr}, eV (experiment)	E_{thr}, eV (theory)
1	W	293	160	175 (Ref. 8) 178 (Ref. 9)	201 (Ref. 9) 160 (Ref. 10) 209, 37 (Ref. 9)
2	W + C	78–293	150		
3	WC			171 (Ref. 9) 150 (Ref. 8)	
4	W oxide	293	65	$<$18 (Ref. 1)	

The threshold energy for sputtering of tungsten oxide by deuterium ions measured by field-ion microscopy is 65 eV, as compared to $E_{thr}\approx18$ eV for tungsten oxide sputtered by D^+ ions in a vessel with a residual oxygen pressure of 8×10^{-5} Torr measured by weighing. As noted in the reference, the low value of E_{thr} is caused by a low binding energy ($E_c=0.3$ eV) of the tungsten oxide molecules to the surface.[1] In our experiments, an oxide film with a thickness of ~50 nm developed on the tungsten surface. An estimate of the binding energy analogous to that in Ref. 1 gives ~1.1 eV.

The substantial increase in the threshold energy for sputtering of a tungsten oxide layer by deuterium ions observed by the new method employed here may also be related to differences between these two methods (weighing and field-ion microscopy). The new method identifies only the vacancies in the tungsten, that is, it counts only tungsten atoms,while the weighing method records all sputtered surface species, including adsorbed atoms and molecules.

Auger electron analysis of a mixed W–C layer showed that in a layer with a thickness of $\sim10^4$ nm, the W and C are distributed essentially uniformly, while the oxygen impurity on the surface is no more than 9.5 at. %. The thickness of the layer of WO on the tungsten resulting from heating it in air is ~50 nm.

The energy dependence of the sputtering coefficient for tungsten by deuterium ions obtained in the present experiments is shown in Fig. 5 (curve *1*). Besides these data, Fig. 5 also shows the experimental (curve *2*) and theoretical (curve *3*) energy dependences obtained in Ref. 9. As can be seen from Fig. 5, the tungsten sputtering coefficients measured by

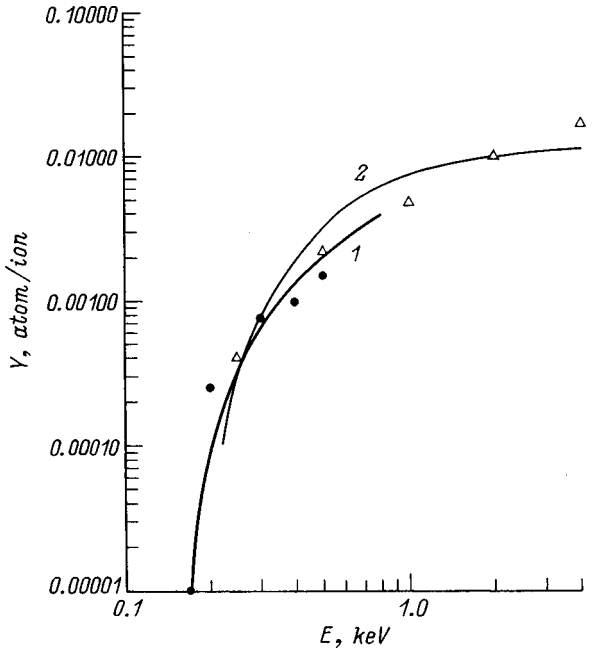

FIG. 6. Energy dependence of the sputtering coefficient of a mixed W– C layer on a tungsten surface for sputtering by D^+ ions: *1* — results of the present work; *2* — experimental data from Refs. 9 and 10 for a WC system.

the different methods are similar and agree fairly well with the theoretical curve.

The energy dependences of the sputtering coefficients for a pulverized layer of W–C and WC[9] are also essentially the same as those obtained here (Fig. 6).

Figure 7 shows the energy dependence of the sputtering coefficient for tungsten oxide with sputtering by deuterium ions (curve *1*). Experimental data from Ref. 1 for tungsten sputtered at an oxygen pressure of 8×10^{-5} Torr (curve *2*) and for pure tungsten (curve *3*) are shown there for comparison. At energies <100 eV, the sputtering coefficients for tungsten irradiated in a high background pressure of oxygen substantially exceed the field-ion microscopy measurements. For $E\geqslant350$ eV the sputtering coefficients for tungsten oxide (curve *2* of Fig. 7) measured by the weighing method approach those for pure tungsten (curve *3*). This means that when the sputtering coefficient increased to 3×10^{-4} atom/ion under the experimental conditions of Ref. 1, the oxide film on the tungsten surface had already been sputtered away by the D^+ ions. In our experiments, a thick film of tungsten oxide was present on the tungsten surface, so that a higher sputtering coefficient was required to sputter it away.

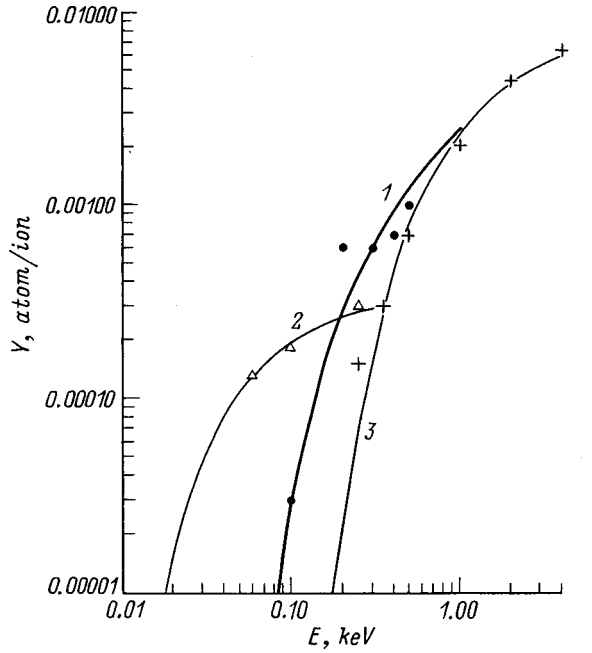

FIG. 7. Energy dependence of the sputtering coefficient of tungsten oxide on the surface of a tungsten sample for sputtering by D^+ ions: *1* — results of the present work, *2* — data of Ref. 9 for tungsten for an oxygen pressure of 8×10^{-5} Torr, *3* — data of Ref. 1 for pure tungsten.

CONCLUSION

1. It has been shown that measuring the sputtering coefficients of materials by field-ion microscopy has the following advantages: the ability to clean the sample surfaces of adsorbed atoms and molecules, of oxide films, etc., directly in the field-ion microscope and the possibility of observing and identifying each vacancy produced by the bombarding ions on the sample surfaces, i.e., the possibility of counting each sputtered atom.

2. A sharp increase has been found in the threshold energy for sputtering of tungsten oxide by deuterium ions. E_{thr} is 65 eV.

3. The threshold energy for sputtering of pure tungsten by deuterium ions at room temperature is in satisfactory agreement with the calculations of Ref. 1, but is considerably lower than the corresponding values determined by the weighing method at room temperature.

4. The energy dependences of the sputtering coefficients of pure tungsten and of a W–C mixed layer on tungsten for sputtering by deuterium ions are in agreement with previously published data for W and WC.

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