SOVIET PHYSICS JETP VOLUME 33, NUMBER 4 OCTOBER 1971

MECHANISM OF FORMATION OF THE ION COMPONENT IN CATHODE SPUTTERING OF METALS

V. I. VEKSLER and B. A. TSIPINYUK

Tashkent State University

Submitted September 18, 1970

Zh. Eksp. Teor. Fiz. 60, 1393–1398 (April, 1971)

The features of the physical schemes of cathode sputtering of metals (CSM) are discussed with the purpose of elucidating the mechanism of formation of the ion component of the process. The experimental energy spectra for sputtered neutral atoms produced upon bombardment of a molybdenum target by mercury ions are compared with the energy spectra for the ion component presented in [16]. The results are not consistent with the "kinetic ion emission" mechanism[9] but are in accord with another mechanism determined by the nonadiabatic nature of the motion of the sputtered particle with respect to the target surface.[6]

In spite of the fact that the ion component of cathode sputtering of metals (CSM) has been under study for a relatively long time[1] and there are a large number of experimental works devoted to its investigation, the question of the mechanism of the occurrence of the ion component of the cathode sputtering of pure metals has so far remained open.

The experimentally known[1-4] values of the coefficient of the ion component of CSM $K_i(\sim 10^{-2}-10^{-4})$ exceed by 10^7-10^9 times the values calculated with the aid of the Saha-Langmuir formula, which pertains to the surface ionization that occurs in thermodynamic-equilibrium conditions. On the other hand, as follows from the latest data,[5] the sputtering of atoms of metal in the ionized state takes place also in the case of an atomically pure surface, so that references to the effect that the appearance of the ion component always has a purely chemical character, connected with the knockout of the ions from the dielectric surface contaminants, are also inconsistent. Attempts to explain the value of K_i within the framework of the Saha-Langmuir-Dobretsov theory[3] were also unsuccessful.

By now, two mechanisms have been proposed for the occurrence of the ion component of CSM. In the first of them, the deviation from the Saha-Langmuir formula is connected with the deviation of the conditions of motion of the sputtered atom from strictly-adiabatic conditions.[6-8] The advocates of the second mechanism[9-12] believe that the appearance of the ion component in CSM is due to the inelastic energy loss in collisions of atoms in the solid ("kinetic ion emission"). Information that makes it possible to draw conclusions concerning the validity of either of these mechanisms can be drawn from an experimental comparison of the energy spectra of the ionic and neutral products of the CSM. This indeed was the purpose of the present study.

For experimental determination of the energy spectra of sputtered neutral atoms we used basically the instrument and procedure described in [13]. We investigated the energy spectra of sputtered Mo atoms on bombardment of a polycrystalline molybdenum target (type III [14]) by Hg^+ ions from a plasma; the ions were normally incident on the surface of the target. The sputtered atoms of the target material were ionized by electron impact in a low-pressure plasma.

The energies of the produced atoms were then investigated by the method of a planar retarding field with subsequent separation by masses in a mass spectrometer. The energy analysis was carried out with respect to one component of the velocity of the sputtered atoms, but the geometry of the analyzer ensured deviation of the investigated part of the energy from the total energy by not more than 1%. To prevent a scattering ion-optical action of the plasma-bounding electrode 11 (see Fig. 1 of [13]), it was constructed in the present modification of the instrument in the form of a palladium-coated copper grid with 9×10^4 openings of 1 mm² each. The energy of the bombarding ions ϵ_0 could range from 300 to 1300 eV. The current density of the primary ions to the target was ~ 2.5 mA/cm² at all energies of the primary ions. As shown by an investigation of the mass composition of the plasma particles, the main component of the residual gas (if we disregard Hg) was $CO(N_2)$ with partial pressure $\sim 1-2\%$ of the pressure of the Hg vapor. The concentration of the Hg^{++} ions was at the level of 2% of the concentration of the Hg^+ ions. The angle ψ_0 between the direction of motion of the primary ions prior to the collision with the target and the direction of registration of the sputtered atoms was 120°. The registration of the ions after their passage through the narrow slit at the exit from the mass spectrometer[13] was with the aid of a copper-beryllium multiplier of the open type (VEU-OT-8M).

When the mass spectrometer magnetic field was tuned to the peak of the Mo^+ ions and the sputtering voltage U_0 was turned off, the multiplier registered the background current I_b (due possibly to plasma atoms diffusely reflected from the walls of the mass-spectrometer tube); this current is independent of the retarding voltage U_{ret}. A suitable procedure was developed for measuring the energy spectrum of the sputtered Mo atoms, with account taken of the dependence of the background current I_b on U_{ret}, which appears when U_0 is turned on.

Figure 1 shows the experimentally obtained energy spectra of sputtered neutral Mo atoms for a number of

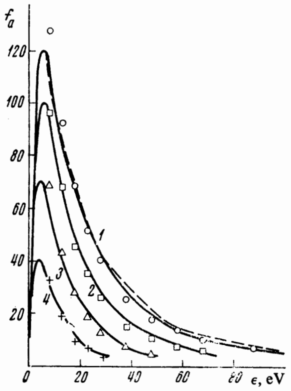

FIG. 1. Experimental and theoretical energy spectra $f_a(\epsilon)$ of sputtered neutral Mo atoms upon bombardment of a molybedenum target by Hg^+ ions (ψ_0 = 120°) for the following values of ϵ_0 (eV): 1–1300, 2–800, 3–500, 4–300. Lines–theoretically calculated spectra [15]: solid–Hg^+–Mo, dashed–Cs^+–Mo.

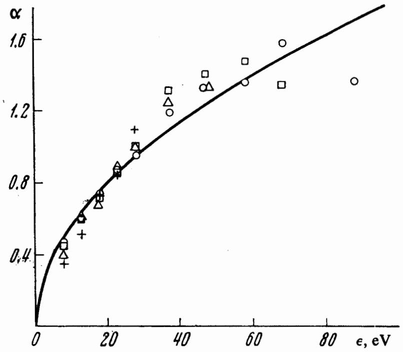

FIG. 2. Plot of $\alpha(\epsilon)$ for the Cs^+–Mo pair, obtained with the aid of the data of [16]. Experimental points: ○–ϵ_0 = 1300 eV, □–ϵ_0 = 800 eV, △–ϵ_0 = 500 eV, +–ϵ_0 = 300 eV. Solid line–theoretical calculations of $\alpha(\epsilon)$ [6].

primary Hg^+ ion energies. The probable error of the measurement results was 2% for ϵ_0 = 800–1300 eV, 3% for ϵ_0 = 500 eV, and 3–5% for ϵ_0 = 300 eV. The solid lines in the same figure show the spectra of the Mo atoms, calculated theoretically[15] for the same cases.

At the present time the only known energy distributions of sputtered Mo^+ ions obtained under analogous conditions[1)] are those for a molybdenum target bombarded with alkali ions.[16] It was therefore decided, after introducing suitable corrections, to compare the energy spectra of the sputtered ions and of the atoms of the main material of the target for molybdenum bombarded with Cs^+ and Hg^+ ions, respectively.

It follows from Fig. 1 that there is a very good degree of agreement between the theoretical and experimental energy spectra of the sputtered neutral atoms for the case Hg^+-Mo. Recognizing that a similar degree of agreement was observed also for other "bombarding ion + metal" combinations,[15] it can be assumed that such a correspondence should take place also for the case Cs^+-Mo. The dashed line in Fig. 1 shows the theoretically calculated[15] energy spectrum of the Mo atoms sputtered from a molybdenum target by Cs^+ ions of 1300 eV energy. We see that the indicated curve does not differ strongly from the corresponding curve for the case Hg^+-Mo. The same holds true for other energies of the primary ions.

This makes it possible to introduce into the experimentally obtained energy spectra of the sputtered ions, in the case of Hg^+-Mo, theoretical corrections (small in magnitude) corresponding to the transition to the combination Cs^+-Mo. Then, using the data of [16], we can find the ratio $\alpha(\epsilon)$ of the energy spectra of the ionic and neutral products in the sputtering of a molybdenum target by Cs^+ ions. Figure 2 shows the thus-obtained plots of $\alpha(\epsilon)$ for a number of values of the primary-ion energies ϵ_0. It follows from this figure that the shape of the $\alpha(\epsilon)$ curve does not depend on the energy of the primary ions.

In the first of the aforementioned mechanisms for the formation of secondary ions, the function $\alpha(\epsilon)$ is simultaneously the degree of ionization of the particles leaving the surface. A theoretical estimate of the degree of ionization α of an atom moving away from the surface of a metal was carried out in [6]. within the framework of a schematized model, in which the metal and the atom were considered as one-dimensional square potential wells. Account was taken of the change of the potential of the interaction of the electron with the nucleus due to the screening of the latter by the electron cloud penetrating from the metal into the region of the atom. A calculation was made of the nonstationary wave function of the system comprising the metal and the atom moving away from its surface, and the probability flux was determined for the electron going over from the metal to the atom. This has made it possible to find for α the expression

$$\alpha \approx \alpha_0 + 2(1 - \ln 2)\lambda_0 v_\varphi l + [1 + 4(1 - \ln 2)\lambda_0] v_\varphi^2 l^2 / 12, \qquad (1)$$

where α_0 is the degree of ionization after Saha-Langmuir,

$$v_\varphi = 4\mu l y_1^{-1} \hbar^{-2} (e\varphi\varepsilon\mu / m)^{1/2},$$

l, m, and ϵ—respectively, the diameter, mass and kinetic energy of the ion, $\lambda_0 = \sqrt{V_i/\varphi} - 1$—the work function of the metal, V_i--the ionization potential of the atom, μ, e—the mass and charge of the electron, y_1--the first root of the equation

$$\frac{(k_\varphi^2 l^2 + y^2)^{1/2}}{y} \sin y = 1, \quad k_\varphi^2 = \frac{2\mu}{\hbar^2} e\varphi.$$

Formula (1) is valid when $\alpha - \alpha_0 \ll 1$, $e\varphi \leq eV_i < W_a$, where W_a is the depth of the potential well imitating the metal. The use of this formula for an estimate of the value of K_i, for example for the system Cs^+-Mo, shows that $K_i \sim 10^{-2}$, which agrees in order of magnitude with the data of [2].

Resonant neutralization of the ion was also calculated in [7,8], and in [8] it was shown that the well-known formula

$$\alpha = \exp(-\mathrm{const} / \sqrt{\varepsilon}), \qquad (2)$$

which follows from the so-called "approximation of the immobile ion," is logically inconsistent. To solve the problem in question they used in [8] a time-dependent perturbation-theory method. For small ion velocities, in the case when $eV_i < W_a$, the following expression is obtained from formulas (3.13) and (3.14) of [8],

---

[1)] The same values of the energy of the bombarding ions and of the angle between the primary-ion momentum and the direction of registration of the secondary particles.

$$\alpha \approx 1 - \frac{\beta}{\sqrt{\varepsilon}} \geqslant 0 \quad \beta = \frac{64}{15} \frac{e^{10}\mu^{5/2}m^{1/2}a_0(W_a - eV_i)^{3/2}}{\hbar^6 W_a^3}, \tag{3}$$

where a_0 is the Bohr radius. It should be noted that the use of the wave functions of an isolated atom and a metal, as initial wave functions, as is done in [8], is not justified because of the presence of a very intense electron exchange in the metal-atom system in a wide interval of distances between the atom and the metal (~ 10 Å).[17] It is possible that because of this the parameter β calculated in accordance with (3) turns out to be very large (for example, for molybdenum $\beta \approx 6.6 \times 10^3$ (eV)$^{1/2}$) and for low energies $\alpha = 0$.

The gist of the mechanism of kinetic ion emission[9-12] consists in the following. When two atoms collide in a solid, the deformation of their internal electron shells leads to excitation of corresponding electron states. If the energy of the relative motion of the atoms is so large that the perturbed electron states overlap energywise the unoccupied levels of the conduction band, then after the atoms move apart there can be produced a "hole" in the internal shell of one of them (such a mechanism was considered also in [18]). After the lapse of a certain time, the hole recombines with one of the free electrons of the metal via the Auger process. (For example, according to [10], the times of relaxation τ for aluminum and copper are 10^{-14} and 10^{-16} sec, respectively.) If no recombination occurs during the time necessary, in the sputtering of such an "excited" atom, for the atom to leave the metal, then the excited atom outside the metal will go over via the autoionization process into an ionic state with emission of an electron. In accordance with this, the authors of [9-12] regard the presence of a high-energy peak in the energy spectrum of the secondary electrons emitted by the metals of the nontransition group (when they are bombarded by inert-gas ions with energy 10 keV) as experimental proof of the validity of the mechanism proposed by them for the phenomenon.[19] It should be noted that the occurrence of the indicated peak, as proposed by the indicated authors, can also be attributed to interband Auger transitions inside the metal.

If we assume nevertheless that the mechanism of kinetic ion emission plays a definite role at higher energies of the primary ions ($\epsilon_0 \gtrsim 10$ keV), then even general considerations cast doubt on the validity of this mechanism at energies not exceeding 1–2 keV. Indeed, the energy thresholds of the indicated mechanism cannot lie below the thresholds of the kinetic electron-ion emission, which, for example, are respectively 1.6 keV[18] and 2 keV[20] for the systems K^+-W and Cs^+-W. At the same time, the emission of secondary W^+ ions for the indicated cases is observed already at $\epsilon_0 = 100-300$ eV.[5]

It is seen from the foregoing analysis that in the case when the occurrence of the ion component of the CSM is determined by the nonadiabatic character of the motion of the knocked-out atomic particle relative to the surface of the metal, then, as is seen from formula (1), the ratio of the spectra α of the sputtered ions and of the neutral atoms should in the first approximation be proportional to $\sqrt{\epsilon}$ and should be independent of the energy of the primary ions ϵ_0. On the other hand, if the ion component of the CSM is the result of inelastic energy losses upon collision of the atoms in the metal, then the dependence of the probability of excitation of the atoms on the energy of the primary ion and on the collision parameter, and also the fact that the processes responsible for the emergence of excited and neutral atoms from the metal differ in nature (cascade and cascade-focuson[15] collisions, respectively), should lead not only to a dependence of α on ϵ, but also to a substantial dependence on ϵ_0.

The presented theoretical estimate of the deformations of the $\alpha(\epsilon)$ curves with changing ϵ_0 actually confirms these considerations. In particular, the aforementioned dependence of the probability of excitation of the atoms on ϵ_0 and on the collision parameters causes (a) the maximum energies of the secondary ions ϵ_{mi} to be much smaller than the maximum energies of the sputtered neutral atoms ϵ_{ma}, and (b) the ratio $\epsilon_{mi}/\epsilon_{ma}$ to decrease rapidly with decreasing ϵ_0.

The obtained experimental results (Fig. 2) allow us to assume that in the experimentally investigated case the emission of the secondary ions of the main material of the target is due to the nonadiabatic character of the motion of the sputtered atom relative to the surface of the target. For comparison, Fig. 2 shows the theoretical $\alpha(\epsilon)$ dependence calculated from formula (1). The agreement is perfectly satisfactory.

It should be noted that to obtain satisfactory agreement of the general course of the experimental $\alpha(\epsilon)$ dependence with the theoretical one calculated by formula (3), it was necessary to decrease the parameter β quite appreciably (by a factor of 2500). However, even in this case the degree of agreement turns out to be much worse than for formula (1): according to (3), there should be no ions with energy $\epsilon \lesssim 7$ eV among the products of the cathode sputtering, whereas it follows from the experimental data of [16] that it is precisely at $\epsilon \sim 7$ eV that a maximum is observed in the experimental energy spectrum.

The authors are grateful to G. Levik for help with the experiment.

---

[1] V. I. Veksler, Author's abstract of Candidate's Dissertation, Tashkent, 1952; V. I. Veksler, Dokl. Akad. Nauk Uzbek SSR, No. 1, 9 (1956).

[2] V. I. Veksler, Zh. Eksp. Teor. Fiz. **38**, 324 (1960) [Sov. Phys.-JETP **11**, 235 (1960)].

[3] V. I. Veksler and M. B. Ben'yaminovich, Zh. Tekh. Fiz. **26**, 1671 (1956) [Sov. Phys.-Tech. Phys. **1**. 1626 (1957)].

[4] R. Castaing and J.-F. Hennequin, C. R., Paris, **262**, B1008, 1966.

[5] A. A. Adylov, V. I. Veksler, and A. M. Reznik, Izv. AN Uzbek SSR, Seriya Fiz-mat. No. 6, 35 (1970).

[6] V. I. Veksler, Izv. AN Uzbek SSR, Seriya Fiz-mat. No. 4, 34 (1959).

[7] Sh. Sh. Shekhter, Zh. Eksp. Teor. Fiz. 7, 750 (1937).

[8] B. A. Trubnikov and Yu. N. Yavlinskiĭ, Zh. Eksp. Teor. Fiz. 52, 1638 (1967) [Sov. Phys.-JETP 25, 1089 (1967)].

[9] P. Joyes and R. Castaing, C. R., Paris, 263, B384 (1966).

[10] P. Joyes and J.-F. Hennequin, J. Phys. 29, 483 (1968).

[11] P. Joyes, J. Phys. 30, 243 (1969).

[12] P. Joyes, J. Phys. 30, 365 (1969).

[13] M. B. Ben'yaminovich and V. I. Veksler, Zh. Tekh. Fiz. 34, 361 (1964) [Sov. Phys.-Tech. Phys. 9, 284 (1964)].

[14] M. B. Ben'yaminovich and V. I. Veksler, Izv. AN SSSR, Seriya Fiz. 28, 1387 (1964).

[15] V. I. Veksler, Fiz. Tverd. Tela 11, 3132 (1969) [Sov. Phys.-Solid State 11, 2540 (1970)].

[16] A. A. Adylov, V. I. Veksler, and A. M. Reznik, ibid. 11, 1779 (1969) [11, 1441 (1970)].

[17] V. I. Veksler, Dokl. Akad. Nauk Uzbek SSR No. 5, 3 (1955).

[18] N. N. Petrov, Fiz. Tverd. Tela 2, 940 (1960) [Sov. Phys.-Solid State 2, 857 (1960)].

[19] J.-F. Hennequin, J. Phys. 29, 1053 (1968).

[20] I. A. Abroyan, M. A. Eremeev, and N. N. Petrov. Usp. Fiz. Nauk 92, 105 (1967) [Sov. Phys.-Usp. 10, 332 (1967)].

Translated by J. G. Adashko
153