# Secondary ion emission during sputtering of polycrystalline copper

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The energy spectra of secondary $Cu^+$ and $Na^+$ ions produced by ion bombardment of polycrystalline copper were studied experimentally and theoretically as a function of the angle of emission and the vacuum conditions in order to determine the ionization mechanisms. It is shown that emission from a "clean" surface is described by an electron-tunneling model and emission from an oxidized surface is described by a bond-breaking model.

## 1. INTRODUCTION

The bombardment of the surface of a solid with an ion beam is accompanied by sputtering of particles which leave the surface in different charge states. Secondary ion emission, which is employed, in particular, in secondary-ion mass spectrometry (SIMS), is of great practical interest for surface analysis. This method, however, is still semiquantitative, since a single comprehensive theory of secondary-ion emission (SIE) does not exist.[1-3] The theory of SIE for oxides is even less well developed, though it too is of great practical interest. Oxidation of the surface of a metal can increase the SIE efficiency and therefore the sensitivity of methods employing SIE by two to three orders of magnitude.[4]

A serious obstacle to the construction of a theory of SIE is the lack of reliable experimental data on the mechanisms of the emission of secondary ions. The best way to check the effectiveness of one or another model of SIE is to study the energy spectra of secondary ions at different angles of emission $\theta$. The published work on the energy spectra of secondary ions for different values of $\theta$ gives contradictory results and does not permit determining the mechanisms responsible for the deformation of the energy spectra.[5-8] The present paper gives the first results of such studies for polycrystalline copper for a wide range of vacuum conditions. Theoretical analysis of the results obtained permits a number of conclusions to be drawn regarding the mechanisms of SIE and some numerical estimates to be made.

## 2. EXPERIMENTAL PROCEDURE

The mechanisms of SIE were studied using an arrangement consisting of an Ardenne duoplasmatron ion source, a magnetic separator for the primary beam, and the sample chamber. The specially developed measurement system consisted of a rotating energy analyzer and a stationary mass analyzer; this makes it possible to study secondary ions emission as a function of angle, energy, and mass. Figure 1 shows a diagram of the measuring system. The beam of primary ion $I_p^+$ was directed onto the target $M$ along the axis $O_1$. The target could rotate around the axis $O_1$; this made it possible to vary the azimuthal observation angle over a range of 360°. The energy analyzer (EA), consisting of 180- and 90-degree spherical copper deflectors (SDs) and electrostatic lenses L1–L3, was placed on a platform that could rotate around the axis $O_2$, which was also the optical axis of the mass spectrometer and passed through the center of the incident beam on the surface of the target. The standard APDM-1 mass spectrometer (MA) and secondary-electron multiplier (VÉU-6) were rigidly fastened to the flange of the chamber. This geometry made it possible to perform independent measurements of the azimuthal or polar distributions of the secondary ions. The angle $\theta$ (measured from the normal to the surface) at which the secondary ions were recorded could be varied from $\theta_{\min} = 19°$ to $\theta_{\max} = 90°$.

The angular resolution was determined by the diaphragms of the adjustable input cone and was equal to 2–10°. Energy scanning was performed by acceleration (deceleration) of the secondary ions in the lens L1. The spherical deflector was adjusted to a constant transmission energy $E_0 = 20$ eV; this ensured that the transmission bandwidth of the energy analyzer was constant $\Delta E = 1.4$ eV. The transmission coefficient of the system remained constant while scanning in the energy range from 2 to 200 eV. The working vacuum in the chamber was equal to $10^{-8}$ Torr. The sample consisted of 99.99% pure polycrystalline copper. The sample was bombarded along the normal to the surface with a beam of 4 keV $Ar^+$ ions with a current density of $10^{-5}$ A/cm$^2$. To study the dependence of the SIE on the residual-gas pressure air could be injected into the sample chamber in a controlled fashion. The entire system as a whole and each separate part of the system were calibrated with the help of a source of thermal $Li^+$ ions.

## 3. SECONDARY ION EMISSION UNDER CLEAN CONDITIONS (EXPERIMENT AND DISCUSSION)

Theoretical models of SIE from metals can be divided into two basic groups. In one group the process of tunneling of an electron from the undisturbed surface to the emitted particle is studied.[9-11] The other group is predicted on the existence of a local region in thermodynamic equilibrium, created by a series of collisions, with a high electron temperature, which determines the probability of the formation of an ion.[12,13] Both classes of theory study the interaction of a particle departing from the surface of a solid that basically consists of the electron gas of the metal. When the surface of the metal is oxidized electronegative oxygen binds an electron of the metal and the process of charge exchange accompanying emission of a particle acquires a binary character. In this case the approaches indicated above are no longer admissible. In Ref. 14 it was proposed that the bond-breaking model be employed to explain SIE from ionic crystals. This approach was later developed in Refs. 15 and 16 in order to determine the degree of ionization of particles sputtered from oxides, i.e., for the case of bond breaking in the metal-atom–oxygen-atom system.

As we have already pointed out above, oxidation of the

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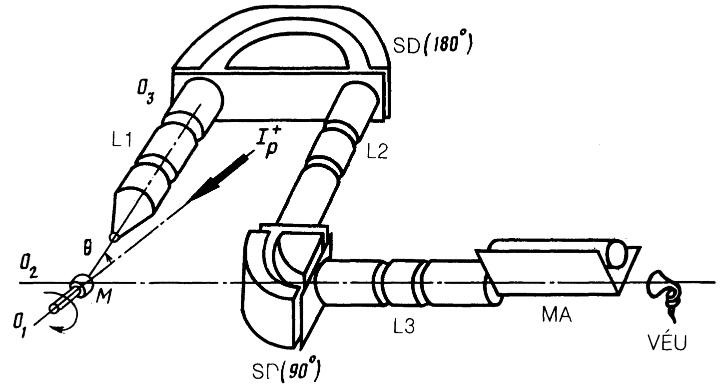

FIG. 1. Diagram of the measuring system.

surface sharply increases the secondary emission of positive ions. The experiment determines how much of the surface of the sample was covered with oxygen from the residual pressure in the working chamber. Figure 2 shows how the yield of positive $Cu^+$ and $Na^+$ ions depends on the residual-gas pressure in the sample chamber. At pressures below $p = 10^{-7}$ Torr the yield of $Cu^+$ ions remains virtually constant; this corresponds to working with copper under "clean" conditions. The fact that for impurity Na the yield does not depend on the pressure suggests that sodium is already bound to oxygen.

Thus the results of investigations of secondary emission from polycrystalline copper under pressures corresponding to clean conditions can be used to analyze the applicability of different models of SIE. Figure 3 shows $Cu^+$ energy spectra for different observation angles $\theta$. The energy distribution $S^+(E,\theta)$ of the secondary ions is determined by the corresponding distributions of all emitted particles $S^0(E,\theta)$ and the ionization probability $R^+(E,\theta)$, i.e.,

$$S^+(E,\theta)=S^0(E,\theta)\cdot R^+(E,\theta),$$

where $S(E,\theta)$ is the number of secondary particles knocked out at an angle $\theta$ with energy $E$ by one incident ion. The following expression from Sigmund's cascade theory of sputtering[17] is usually employed for $S^0(E,\theta)$:

$$S^0(E,\theta)\propto\frac{E}{(E+u)^3}\cos\theta, \qquad (1)$$

where $E$ is the energy of the secondary particle, $u$ is the binding energy, and $\theta$ is the angle of emission of the particle. According to the theory of electron tunneling[10] the probability of ionization of the sputtered particles is equal to

$$R^+=\frac{2}{\pi}\exp(-v_0/v\cos\theta), \qquad (2)$$

where $v_0 = \pi(I-\varphi)/2\beta b\hbar$; $v$ is the velocity of the particle; $I$ is the ionization potential; $\varphi$ is the work function; $\beta$ is a parameter characterizing the range of the atom-surface interaction; and $b$ is a constant that accounts for the reduction of the difference $I-\varphi$ owing to image forces.

Multiplication by $R^+(E,\theta)$ shifts the position of the maximum of the energy distribution, corresponding to $u/2$ for $S^0(E,\theta)$, into the region of high energies, and the position of the maximum is determined uniquely by the value of $B(\theta)$ (the expression (2) can be written in the form $R^+\propto\exp[-B(\theta)/E^{1/2}]$). Once $B(\theta)$ has been calculated from the energy distribution of the secondary ions $S^+(E,\theta)$ for one observation angle $\theta_0$ the change in the energy spectrum as the angle $\theta$ changes can be traced by observing the position of the maximum of the energy distribution. The value of $B(\theta_0)$ is determined as follows:

$$B(\theta_0)=\frac{(2E-u)}{(E+u)}2E^{1/2}\Big|_{E=E_{max}(\theta_0)},\qquad B(\theta)=B(\theta_0)\frac{\cos\theta_0}{\cos\theta}.$$

Figure 3 shows the experimental and theoretical energy spectra for several values of the angle $\theta$. It is not difficult to see that the chosen mechanism of ionization (see the expression for $R^+$) describes well the shape and position of the maxima of the energy spectra as a function of the angle. The

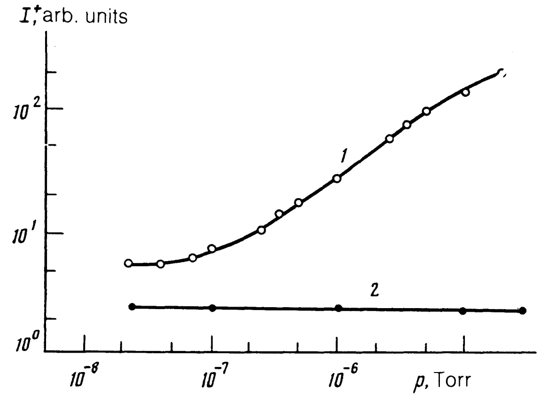

FIG. 2. The intensity of the secondary $Cu^+$ (1) and $Na^+$ (2) ions versus the residual-gas pressure.

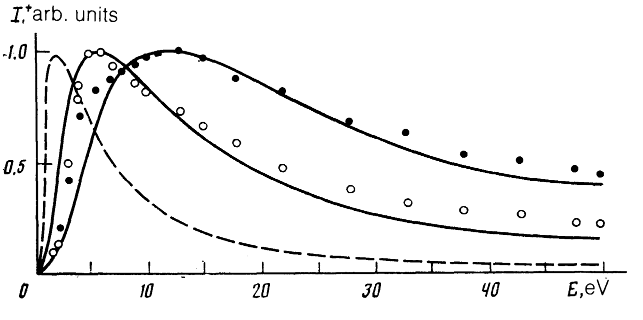

FIG. 3. The energy spectrum of $Cu^+$ ions under clean conditions ($p = 10^{-8}$ Torr) for different emission angles $\theta$. The experimental points correspond to the values $\theta = 19°$ (○) and 63° (●). The solid curves show the calculation for $Cu^+$ ions and the broken curve shows the calculation for $Cu^0$ atoms.

change in the position of the maximum of the energy distributions agrees with the results of Refs. 6 and 7 for Al and corresponds to shifts of the maximum toward high energies as the emission angle is increased.

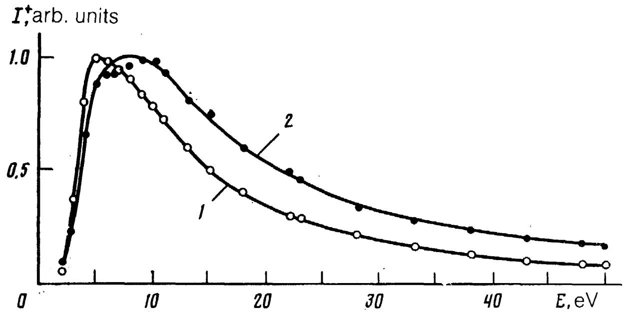

FIG. 4. The energy spectrum of secondary Cu$^+$ ions for an oxidized copper surface ($p = 5\cdot10^{-6}$ Torr). The observation angle $\theta = 19°$ (1) and 63° (2).

Note that according to the other class of theories of SIE from metals,[12,13] which give a dependence of the form $R^+ \propto v^n(\cos\theta)^m$, the shape of the energy spectrum should be independent of the angle $\theta$, just as for any other mechanism of the type $R^+(E,\theta) = f(E)g(\theta)$, i.e., admitting separation of the variables $E$ and $\theta$. Neither type of theory, however, gives the correct numerical value of $R^+$ and both groups give values that are much too high (often by two to three orders of magnitude).

## 4. SECONDARY ION EMISSION FROM AN OXIDIZED SURFACE

At pressures $p \geqslant 5\cdot10^{-6}$ Torr the surface atoms of polycrystalline copper are bound with oxygen (Fig. 2). The bond is ionic. The emission of Cu$^+$ is determined by the probability of electronic charge exchange at the point of pseudocrossing of the quasimolecular terms Cu$^+$–O$^-$ and Cu–O. At this point the difference $I - A$ of the energies of the terms at infinity is equal to the Coulomb interaction energy, i.e., $I - A = R_0^{-1}$, where $A$ is the electron affinity of O$^-$ and $R_0$ is the distance between the particles (here and below the atomic system of units is employed: $m_e = \hbar = e^2 = 1$).

To determine the probability of charge exchange we shall employ the Landau-Zener model.[18,19] According to this model the probability of a transition at the point of pseudocrossing of the terms is given by

$$P^+ = \exp(-2\pi V_{12}^2/v|F|)\,|_{R=R_0}, \tag{3}$$

where $V_{12}$ is the matrix element of the exchange interaction

$$V_{12} = \langle \Psi_1 | H | \Psi_2 \rangle,$$

$v$ is the relative velocity of the particles, and $F$ is the difference of the slopes of the diabatic terms at the point $R_0$. The main difficulty lies in determining the term $V_{12}$. The formation and decomposition of negative ions are studied in Ref. 20. The following expression is derived for the matrix element $V_{12}$ at the point $R_0$ of pseudocrossing of the molecular terms:

$$|V_{12}| = \frac{R_0}{8}\chi_1\left(\frac{R_0}{2}\right)\chi_2\left(\frac{R_0}{2}\right),$$

where $\chi_1(r)$ and $\chi_2(r)$ are the molecular radial wave functions of the electron bound to the neutral particle and the negative ion, respectively. Here

$$\chi_2(r) = \left(\frac{R}{R-r}\right)^{1/\gamma}\frac{C(2\gamma)^{1/2}}{r}\exp\left[-\gamma r - \frac{r}{R\gamma}\right],$$

where $\gamma^2/2 = A$ is the binding energy and $C$ is the normalization constant of the wave function. For metals with an outer $s$-electron a hydrogen-like wave function can be employed[16]:

$$\chi_1(r) = 2\alpha^{3/2}\exp(-\alpha r),$$

where $\alpha^2/2 = I$ is the ionization energy.

The velocity $v(R_0)$ is related to the observed velocity of the particle $v(\infty)$ as follows:

$$v(R_0) = [v^2(\infty) + 2(I-A)/m]^{1/2},$$

$$|F| = \left|\frac{d(E_1^0 - E_2^0)}{dR}\right|_{R_0} = R_0^{-2} = (I-A)^2,$$

since in a neighborhood of the point $R_0$ the diabatic term $E_1^0$ does not depend on $R$, while $E_2^0$ behaves as $R^{-1}$.

Thus in the expression for the charge-exchange probability $P^+$ only the normalization constant $C$ of the radial wave function of the electron $\chi_2(r)$, corresponding to the negative oxygen ion O$^-$, remains unknown. We shall assume that the constant $C$ is the same for bond breaking in the Cu–O and the Na–O systems. Since the total spin of a negative ion is usually equal to zero, a negative ion forms if the spins of the electrons of the interacting atoms are in the singlet state.[20] It follows that the ionization probability is $R^+ = lP^+$, where $l = 1/4$.

Experiments on secondary ion emission from copper under clean conditions yield $R^+ = 10^{-4}$ (Ref. 21). Using this value and the trace of the pressure dependence of the ion yield (Fig. 2) the probability $R^+$ for an oxidized surface and therefore the constant $C$ in the Landau-Zener formula can be determined. It is found that $C = 0.067$. We now know expressions for $R^+_{\rm Cu}(E)$ and $R^+_{\rm Na}(E)$, which have the form

$$R^+(E) = {}^1/_4\exp[-K(I,A)(E+I-A)^{-1/2}]. \tag{4}$$

Using $S^0(E,\theta)$ we can obtain the energy spectra of secondary Cu$^+$ and Na$^+$ ions for an oxidized surface. Figures 4 and 5 show the corresponding experimental spectra. It is understandable that the expression

$$S^+(E,\theta) \propto \frac{E\cos\theta}{(E+u)^3}\exp[-K(I,A)(E+I-A)^{-1/2}]$$

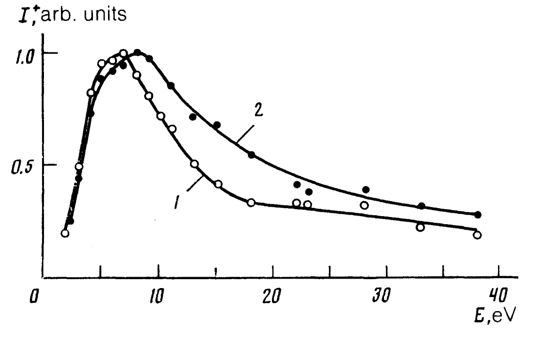

FIG. 5. The energy spectrum of Na$^+$ impurity ions for an oxidized copper surface. The observation angle $\theta = 19°$ (1) and 45° (2).

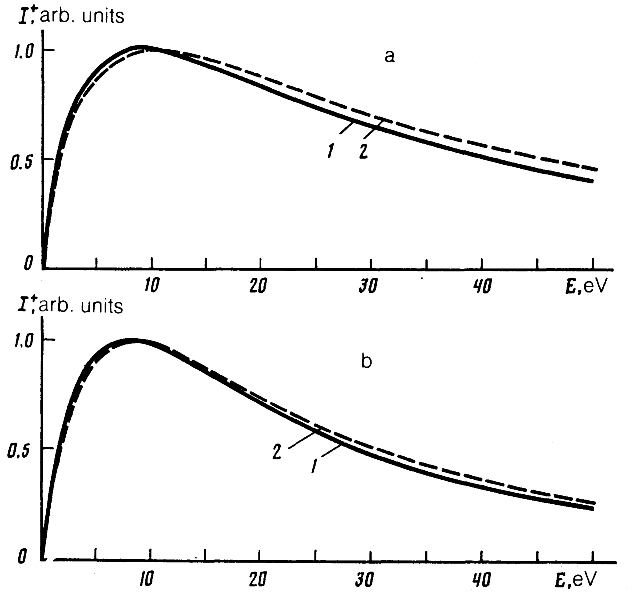

FIG. 6. The calculated energy spectra of secondary ions for an oxidized copper surface: a—$Cu^+$ ions, $\theta = 19°$ (1) and 63° (2); b—$Na^+$ ions, $\theta = 19°$ (1) and 45° (2).

cannot describe the change in the shape of the spectrum as the angle $\theta$ changes, though a small change is observed experimentally (much smaller than for clean conditions). This discrepancy could be connected, in particular, with the simplified choice of the distribution function $S^0(E,\theta)$ of emitted particles in the form (1).

A more general approach[22] taking into account the anisotropy of the development of a succession of collisions for normal incidence of the primary beam leads to the expression

$$S^0(E,\theta) \propto \frac{E\cos\theta}{(E+u)^3}\,[1-3C(E_0)\,(E\cos^2\theta-u)^{1/2}), \qquad (5)$$

where the parameter $C(E_0)$ depends on the energy of the beam $E_0$ (usually $\propto E_0^{-1/2}$), the ratio of the masses of the primary and secondary particles, and the manner in which the collision cascade is initiated. As shown in Ref. 23 many experiments on the spatial distribution of secondary ions can be explained only on the basis of this approach. Using the expression (5) for $S^0(E,\theta)$ changes the position of the maximum of the energy spectrum somewhat (Fig. 6) as the angle of emission $\theta$ changes; the direction of the change corresponds to that observed experimentally: for $\theta_1 > \theta_0$

$$E_{max}(\theta_1) > E_{max}(\theta_2).$$

Another factor that leads to a change in the form of the energy spectrum as the angle $\theta$ changes is connected with the fact that $R^+(E)$ $(P^+(v))$ depends on the radial component of the relative velocity of the interacting particles at the point $R_0$. For a fixed orientation of the bond and constant velocity $v(\infty)$ the value of $v_R(R_0)$ depends on the emission angle $\theta$.

A more detailed analysis of the process of emission of secondary ions, as we can see, shows that the form of the energy spectrum of the ions does depend on the observation angle $\theta$. Thus the bond-breaking model gives good qualitative agreement with experiment in describing SIE from an oxidized surface of a metal. In addition this model also gives a numerical value for $R^+(E)$ that is in agreement with existing experimental data; this is especially valuable for practical applications. For Na we obtain $R^+(6\text{ eV}) = 1.5\cdot10^{-1}$, which agrees well with the value $R^+(6\text{ eV}) = 2.5\cdot10^{-3}$ for Cu, taking into account the relative concentration of impurity Na in the sample, the transmission coefficient of the system, the coefficient of sputtering, and the relative average intensity of the $Na^+$ and $Cu^+$ signals in the mass spectrum.

Comparing the experimental and theoretical spectra also makes it possible to evaluate the binding energy of the Na atom with the surface; it turns out that it is equal to approximately 11–13 eV. According to Ref. 24 the binding energy of a metal atom for an oxidized surface can be much greater than the corresponding value for a clean surface. In particular, $u = 12.3$ eV for Ca. Since the coefficients of sputtering of copper from the oxide and pure copper are virtually identical[24] we used the same value of $u$ in both cases.

## 5. CONCLUSIONS

The experiments on secondary ion emission from copper under clean conditions show that the theory of electron tunneling describes well the form of the secondary-ion energy spectrum. The position of the maximum of the energy distribution as a function of the emission angle $\theta$ of the particles is also described by this theory and corresponds to $E_{max}$ increasing as a function of $\theta$. This theory presupposes that the departing particle interacts with the surface of the solid as a whole, so that the component of the velocity normal to the surface, $v = v\cos\theta$, enters into the expression (2) for $R^+$; this leads to a corresponding dependence on $\theta$. However this theory gives numerical values that are much too high (by two to three orders of magnitude). We believe that this is attributable to the very rough description of the location of the ground state of the emitted particle as a function of the distance to the surface.[9,10]

For an oxidized surface secondary ion emission is described by the Landau-Zener formula using for the electron the radial wave functions obtained in Ref. 20. This formula contains one undetermined constant—the normalization constant $C$ of the wave function of the electron bound to the negative ion $O^-$. To a lowest order it may be assumed that this constant is the same for binding of oxygen with different metals. The constant can be determined either from the pressure dependence of $R^+$ if the value of $R^+$ for clean conditions is known or from the position of the maximum of the energy spectrum of secondary ions if the binding energy for the oxide is known. Knowing the constant and using the asymptotic expansion of the wave functions of the electron for a neutral particle we can determine $R^+(E)$ for different metals. In the analysis of solid surfaces this makes possible quantitative measurements by the method of secondary-ion mass spectrometry at pressures corresponding to maximum sensitivity of the method.

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