Formation of the final charge state of particles sputtered by an ion beam from a solid surface in the case of resonant transitions

I. A. Bandos, Yu. V. Slyusarenko, A. Yu. Sobolev, and A. G. Kova'
Kharkov State University, 310077 Kharkov, Ukraine

(Submitted 12 October 1994)
Pis'ma Zh. Eksp. Teor. Fiz. **60**, No. 9, 655–658 (10 November 1994)

The probability for ionization of a sputtered ion as it moves away from the surface is analyzed in the case of resonant atom–solid transitions. In this case it is possible to derive explicit solutions for a realistic energy-density function of the electron states, rather than exclusively for a model function as in the case of nonresonant transitions. Expressions are given for the ionization probability in two model cases. The behavior of this probability as a function of the velocity of the escaping ion is different from that in the case of nonresonant transitions. © *1994 American Institute of Physics.*

One of the most informative methods for studying the interaction of an ion beam with a solid surface is secondary-ion mass spectrometry (SIMS). This method is capable of highly accurately determining the mass and energy spectra and the angular distributions of the secondary charged particles sputtered from the target surface. If the data obtained by this method are to be used successfully to study surfaces, it is necessary to construct models which are capable of explaining the observed characteristics of the sputtered particles and of relating these characteristics to the properties of the surface under study. Here an important role is played by research on the processes by which the final charge state of the sputtered secondary particles is formed.

Most models which describe the formation of the final charge state as a sputtered ion escapes from a surface[1–5] are based on the Andersen Hamiltonian

$$H=\sum_k \epsilon_k c_k^+ c_k+\epsilon_\alpha(t)c_\alpha^+ c_\alpha+\sum_k (V_{k\alpha}c_k^+ c_\alpha+V_{k\alpha}^* c_\alpha^+ c_k). \tag{1}$$

Here the operators c_α^+ (c_α) and c_k^+ (c_k) create and annihilate an electron in a valence orbital of the departing atom[1)] and in the conduction band of the solid in the state,[2)] respectively, $\epsilon_\alpha(t)$ and ϵ_k are the energies of these states; and $V_{k\alpha}(t)$ is an exchange integral which describes electron transitions from the atom to the solid and vice versa. The energy of the electron in the atom, $\epsilon_\alpha(t)$, depends on the distance from the atom to the surface, varying from ϵ_α^0 at $t=0$ (this value corresponds to one of the allowed levels for electrons of the solid) to the value ϵ_α^∞ as $t\to\infty$ (this is the energy of an electron in a valence level of the isolated atom).

We have previously studied[4,5] a model for electron exchange between an atom and a surface based on a Hamiltonian of the type in (1). We placed more emphasis than in some earlier papers[1–3] on correctly constructing the ground state and the Fock space of

the system at finite temperatures. We also considered (outside perturbation theory) nonthermal excitation of the electron subsystem caused (ultimately) by the effect of the primary beam.

It was assumed in Ref. 5, as in some earlier papers,[1-3] that the exchange integral $V_{k\alpha}(t)$ was independent of k, i.e., that the probability amplitudes for the transition of an electron from the atom to the solid were the same for any state k (an extremely nonresonant exchange). Although that model leads to completely satisfactory results for several metals,[5] the assumption that $V_{k\alpha}$ is independent of k is generally a rather serious limitation, and in several cases it may be inappropriate.

In the present letter we consider a generalization of the model proposed in Ref. 5 to the case of the much less restrictive assumption that $V_{k\alpha}$ can depend on the energy difference between the atomic level and the corresponding level of the solid:

$$V_{k\alpha}(t)=W[\epsilon_k-\epsilon_\alpha(t)]u(t). \tag{2}$$

The factor $u(t)$ describes the decrease in the amplitude of the transitions as the atom moves away from the surface.

Skipping over all the details involved in a description of the system at finite temperatures, and skipping over the derivation of the equation describing the dynamics of the system (see Ref. 5 in this regard), we immediately examine the most important results.

The probability that there is no electron in the valence level of the sputtered atom at $t=\infty$ (the ionization probability) is given by

$$R_\alpha(\infty)=[1-f(\epsilon_\alpha^0)]|\lambda_\alpha(\infty)|^2+\int d\epsilon\rho(\epsilon)[1-f(\epsilon)]|\lambda_s(\infty,\epsilon)|^2, \tag{3}$$

where $f(\epsilon)\equiv\{1-\exp(\epsilon-\epsilon_F/kT)\}^{-1}$ is the Fermi distribution function (T is the temperature, and ϵ_F the Fermi energy of the target), $\rho(\epsilon)$ is the energy density of states of the electron levels of the solid, and the quantities $\lambda_\alpha(t)$ and $\lambda_s(t,\epsilon)$ are coefficients of the function in the expression

$$\tilde{c}_\alpha^+(t)=\lambda_\alpha(t)\tilde{c}_\alpha^+(0)+\sum_k \lambda_s(t,\epsilon_k)\tilde{c}_k^+(0). \tag{4}$$

This expression is the solution of the integrodifferential equation describing the dynamics of the system:

$$i\hbar\frac{d\tilde{c}_\alpha^+(t)}{dt}=\sum_k W[\epsilon_k-\epsilon_\alpha(t)]u(t)\exp\left(-\frac{i}{\hbar}\epsilon_k t\right)\exp\left(\frac{i}{\hbar}\int_0^t d\tau\epsilon_\alpha(\tau)\right)\tilde{c}_k^+(0)$$

$$-\frac{i}{\hbar}\int_0^t d\tau\exp\left(\frac{i}{\hbar}\int_\tau^t d\eta\epsilon_\alpha(\eta)\right)Q(t,\tau)u(\tau)u^*(\tau)\tilde{c}_\alpha^+(\tau). \tag{5}$$

Here

$$\tilde{c}_\alpha^+(t)=\exp\left(\frac{i}{\hbar}\int_0^t d\tau\epsilon_\alpha(\tau)\right)c_\alpha^+(t), \tag{6a}$$

$$\tilde{c}_k^+(t)=\exp\left(\frac{i}{\hbar}\,\epsilon_k t\right)c_k^+(t), \tag{6b}$$

and

$$Q(t,\tau)\equiv\int d\epsilon\rho(\epsilon)\exp\left\{-\frac{i}{\hbar}\,\epsilon(t-\tau)\right\}W[\epsilon-\epsilon_\alpha(t)]W^*[\epsilon-\epsilon_\alpha(\tau)]. \tag{7}$$

Equation (5) is derived from the equations of motion [which are determined by Hamiltonian (1)] after the operators $c_k^+(t)$ are eliminated from them.

Solving Eq. (5) in the general case requires numerical methods. There are, on the other hand, two important limiting cases in which analytic solutions can be found. The first is the case of extremely nonresonant exchanges, $W[\epsilon_k-\epsilon_\alpha(t)]=\text{const}$, which has been taken up previously.[4,5] That case has an analytic solution for certain functions $\rho(\epsilon)$ [e.g., for an infinite and uniform band, $\rho(\epsilon)=\text{const}$].

In this letter we consider another case: resonant exchange, with

$$W[\epsilon_k-\epsilon_\alpha(t)]=V(\epsilon_k)\,\delta[\epsilon_k-\epsilon_\alpha(t)]. \tag{8}$$

Expressions (2) and (8) mean that the only transitions possible are those in which the energy of the electron is conserved. The dependence $V(\epsilon_k)$ means that the transition amplitude may be different for different states k.

Equation (5) now becomes a differential equation and can be solved explicitly. This solution is of the form in (4) with

$$\lambda_\alpha(t)=\exp\left\{-\frac{1}{2\hbar^2}\int_0^t d\tau\,\frac{\rho[\epsilon_\alpha(\tau)]}{|\epsilon_k'(\tau)|}|V[\epsilon_\alpha(\tau)]u(\tau)|^2\right\}, \tag{9a}$$

$$\lambda_s(t,\epsilon)=-\frac{i}{\hbar}\int_0^t d\tau W[\epsilon-\epsilon_\alpha(\tau)]u(\tau)\exp\left(-\frac{i}{\hbar}\,\epsilon\tau\right)\exp\left\{\frac{i}{\hbar}\int_0^\tau d\eta\epsilon_\alpha(\eta)\right\}$$

$$\times\exp\left\{-\frac{1}{2\hbar^2}\int_\tau^t d\eta\,\frac{\rho[\epsilon_\alpha(\eta)]}{|\epsilon_k'(\eta)|}|V[\epsilon_\alpha(\eta)]u(\eta)|^2\right\}. \tag{9b}$$

Substituting these expressions into (3) yields the ionization probability $R_\alpha(\infty)$. An important distinctive feature of the resonant case is that the expression for $R_\alpha(\infty)$ can be derived without imposing any restrictions on the energy-density function of the states, $\rho(\epsilon)$, so it is possible to use not only model functions $\rho(\epsilon)$ (as in the case of nonresonant transitions), but also realistic functions to study the ionization of the atom as it moves away from targets with various band structures.

As an example, we write the expressions for the ionization probability for two important cases. The case of an infinitely wide uniform band serves as a model of a metal target (this case was studied in Ref. 5 for nonresonant exchange). We assume

$$\rho(\epsilon)=\rho_0=\text{const} \tag{10}$$

and

$$V(\epsilon)=V=\text{const},\quad u(t)=\exp(-\gamma v t), \tag{11}$$

$$\epsilon_\alpha(t)=\epsilon_\alpha^\infty+(\epsilon_\alpha^0-\epsilon_\alpha^\infty)\exp(-\kappa v t),$$

where v is the velocity at which the atom moves away, along the normal to the surface. A solution of Eq. (5) exists in this case if $\kappa<2\gamma$. The ionization probability at $T=0$ is then

$$R_\alpha(\infty)=\begin{cases}0, & \epsilon_\alpha^0<\epsilon_\alpha^\infty<\epsilon_F,\\ \exp\left\{-\left(\dfrac{\epsilon_F-\epsilon_\alpha^\infty}{\epsilon_\alpha^0-\epsilon_\alpha^\infty}\right)^{\frac{2\gamma}{\kappa}-1}\dfrac{v_0^2}{v^2}\right\}, & \epsilon_\alpha^\infty<\epsilon_F<\epsilon_\alpha^\infty\\ 1, & \epsilon_F<\epsilon_\alpha^0<\epsilon_\alpha^\infty,\end{cases} \tag{12}$$

where

$$v_0^2\equiv\frac{\rho_0|V|^2}{\kappa(2\gamma-\kappa)\hbar^2(\epsilon_\alpha^0-\epsilon_\alpha^\infty)}. \tag{13}$$

The second case is described by the function $\rho(\epsilon)$ with a band gap:

$$\rho(\epsilon)=\begin{cases}\rho_0, & \epsilon<\epsilon_g^{(l)},\\ 0, & \epsilon_g^{(l)}<\epsilon<\epsilon_g^{(h)},\\ \rho_0, & \epsilon>\epsilon_g^{(h)}.\end{cases} \tag{14}$$

It serves as a model of a semiconducting or insulating target (here we have $\epsilon_g^{(l)}<\epsilon_F<\epsilon_g^{(h)}$, and ϵ_α^0 cannot lie in the band gap). For this case the ionization probability is

$$R_\alpha(\infty)=\begin{cases}0, & \epsilon_\alpha^\infty<\epsilon_g^{(l)},\\ \exp\left\{-\left(\dfrac{\epsilon_g^{(l)}-\epsilon_\alpha^\infty}{\epsilon_\alpha^0-\epsilon_\alpha^\infty}\right)^{\frac{2\gamma}{\kappa}-1}\dfrac{v_0^2}{v^2}\right\}, & \epsilon_\alpha^\infty<\epsilon_g^{(l)},\\ 1, & \epsilon_\alpha^0>\epsilon_g^{(h)},\\ & \epsilon_\alpha^\infty>\epsilon_g^{(l)}.\end{cases} \tag{15}$$

It is not difficult to derive expressions for the ionization probability for nonzero temperatures (by following, for example, Appendix D in Ref. 5), but the results are rather complicated, so we will not reproduce them here.

In contrast with the case of nonresonant exchange, in which $R_\alpha(\infty)$ is a superposition of two exponential functions of the reciprocal velocity,[5] the expressions for the ionization coefficient in the case of resonant exchange, (12) and (15), describe an exponential dependence on the square of the reciprocal velocity.[3)] This distinguishing feature could be utilized in analyzing experimental data in order to determine the type of electron exchange which is realized in the given experiment.

[1)]The atom is being treated as a single-level system.

[2)]The subscript k specifies the states of the electrons of the solid. In general, this subscript corresponds to a set of quantum numbers (the quasimomentum, the spin projection, and the band number).

[3)]It can be shown that this assertion is valid for any $\rho(\epsilon)$.

---

[1] A. Blandin *et al.*, J. Phys. (Paris) **37**, 369 (1976).
[2] G. Blaise and A. Nourtier, Surf. Sci. **90**, 495 (1979).
[3] Z. Sroubek, Int. J. Mass Spectrom. Ion Phys. **53**, 289 (1983).
[4] I. A. Bandos *et al.*, SIMS VIII Abstract Book, 8 Int. Conf. (Amsterdam), 15–20 Sept. 1991, p. 16.
[5] I. A. Bandos *et al.*, Surf. Sci. **296**, 97 (1993).

Translated by D. Parsons