Ionization of Atomic Particles Sputtered from Solids

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(Received 19 May 1980)

The ionization probability of an atomic particle sputtered from a simple substrate system has been analyzed with use of a computer simulation of the sputtering process. The ionization probability was found to have a Boltzmann-like functional form and a quantity called "the effective temperature" T_e could be defined. The value of T_e was found to be in the range of 2000–3500 K. The dependence of T_e on the microscopic parameters of the system has been investigated.

PACS numbers: 79.20.Nc, 79.90.+b

The physical processes which lead to the ionization of particles sputtered from solid-state substrates by impacts of fast ions have been studied in considerable details in recent years. The majority of these studies has been motivated by the need to interpret quantitatively the secondary-ion mass spectra (SIMS) but the problems involved are of wider interest.

To describe the process of ionization, two basic approaches have been suggested. Widely used is the thermodynamical macroscopic approach which starts from the assumption that the sputtering region resembles a dense plasma in local thermal equilibrium (LTE) and describes the process by few phenomenological parameters.[1,2] In the other approach, attempts have been made[3-7] to describe the ionization process in terms of microscopical intra-atomic and interatomic parameters. Unfortunately, the physical models used for the microscopical descriptions were usually severely oversimplified.

In this paper we present a microscopical analysis which uses a relatively simple but more realistic atomic model. The results of the analysis justify the use of the LTE formalism for the description of secondary-ion emission and enable us to correlate the phenomenological LTE parameters with the atomic parameters of the sputtered particle and the substrate.

Most of the microscopic theories with exception of those involving inner-shell excitations (e.g., the kinetic model) start from the time-dependent Anderson Hamiltonian

$$H = \sum_{|k|\leq|k_F|} \epsilon_k C_k{}^\dagger C_k + \epsilon_a(t) C_a{}^\dagger C_a + \sum_k [V_{ka}(t) C_k{}^\dagger C_a + \text{H.c.}], \quad (1)$$

where the subscript k labels states within the conduction band of the substrate, the subscript a labels the localized state on the sputtered atom, ϵ_k and ϵ_a are the corresponding one-electron energies, $V_{ka}(t)$ is the interaction between the conduction electrons and the electron in the localized state $|a\rangle$. In Refs. 5 and 6, the Schrödinger equation with the Hamiltonian (1) was solved under the assumption that ϵ_a is time independent and that $V_{ka}(t)$ depends on the position z outside the surface as $V_{ka}\exp(-\gamma z)$. The resulting ionization probability $R^+ = 1 - \langle C_a{}^\dagger(+\infty), C_a(+\infty)\rangle$ was found to be

$$R^+ = (2/\pi)\exp[\pi(\epsilon_a - \epsilon_F)/\hbar\gamma v], \quad (2)$$

where ϵ_F is the metal Fermi energy and v is the particle velocity. Equation (2) has the functional form expected from the LTE theory and the effective temperature T_e is given by $\hbar\gamma v/k$. By substituting $\gamma = 1.5\ \text{Å}^{-1}$ and $v = 1.9\times10^{14}\ \text{Å/sec}$, which are typical values for a particle of the mass equal to 20 proton masses sputtered with the kinetic energy 40 eV, one gets $T_e = 730$ K. This is a rather low temperature and thus the value of R^+ is unrealistically small and has an unrealistically large dependence on v and on the ionization energy $I = -\epsilon_a$. For example, for the kinetic energy of 40 eV and $\epsilon_F - \epsilon_a = 2$ eV the value of R^+ is equal to 10^{-15} and falls to 10^{-21} for the kinetic energy of 20 eV. These results should be contrasted with experimental values of 10^{-6}–10^{-3}. A remedy of this difficulty by a suitable choice of the time variation of $\epsilon_a(t)$ has been proposed by Nørskov and Lundqvist.[6]

It has been suggested and demonstrated in Ref. 7 that the electronic excitations in the substrate should be properly taken into account when one wishes to discribe realistically a typical ionization process during sputtering. It is obvious that the Hamiltonian (1), which is written in the k representation and can be solved directly only when k is a good quantum number, does not guarantee a proper description of local substrate excitations because any excitation spreads immediately through the whole semi-infinite crystal. More appropriate is the Hamiltonian in the site representation,

$$H=\epsilon_a C_a{}^\dagger C_a+\sum_j[V_{ja}(t)C_j{}^\dagger C_a+\text{H.c.}]$$
$$+\sum_{ij}(t)C_i{}^\dagger C_j, \qquad (3)$$

where $|i\rangle$ and $|j\rangle$ are the electron orbitals localized on the substrate atoms; $|a\rangle$ is the orbital of the sputtered atom; V_{ij}, V_{ia} and V_{ii}, V_{jj}, and ϵ_a are the corresponding transfer integrals and diagonal energies. These matrix elements are functions of the atomic coordinates x_i, y_i, and z_i which in turn depend on the time. The time dependence of the coordinates is described by the classical equations of motion

$$M_i\ddot{x}_i=F_i(x_i,y_i,z_i,x_j,y_j,\ldots), \qquad (4)$$

where M_i is the mass of the atom i and F_i is the total classical interatomic force acting on this atom. The system of the Schrödinger equation with the Hamiltonian (3) and Eqs. (4) have to be solved simultaneously with proper boundary conditions. Then the ionization coefficient $R^*=1-\langle C_a{}^\dagger(+\infty),\ C_a(+\infty)\rangle$ can be evaluated. Details of the calculation are described in Ref. 7.

To make the calculation possible within an acceptable computing time we have chosen a simple model consisting of seven atoms shown in Fig. 1. All particles are assumed to have the same mass equal to 20 proton masses. The atom depicted in Fig. 1 by a shaded sphere will be sputtered away due to the impact of the fast impinging atom which is depicted by a black sphere. The kinetic energy of the bombarding atom is 400 eV. The other atoms shown by empty spheres form the model solid-state substrate. The forces of the classical motion of atoms consist of two parts: the weak, central-directed, attractive force which holds the cluster together, and the repulsive Born-Mayer force between pairs of atoms. The components of the central force are given by the spatial derivatives of the potential function. This potential function is equal to $3.7r^2$ eV Å for $r<4$ Å and has a constant value for $r\geqslant 4$ Å, where r is the distance from the center of the cluster. The repulsive force is given by the spatial derivatives of the potential $1.45\times10^5\exp(-3.5\,r_{ij})$ eV Å, where r_{ij} is the distance between the atoms i and j. To simulate, at least partly, the fact that the substrate should be semi-infinite we assume that the next substrate atoms (not shown in Fig. 1) are fixed at their positions. They act only through their repulsive forces and prevent forward sputtering. All these forces stabilize the interatomic distances at values marked in Fig. 1 in Å. It turns out that the general behavior of the ionization probability is insensitive to the choice of the interatomic potential. We use a very hard potential to keep the interatomic distances large so that approximate expressions for electron transfer integrals are applicable.

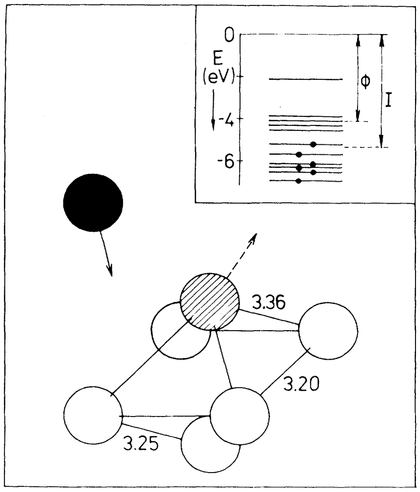

FIG. 1. The atomic model used in the computer simulation. The model consists of the atomic substrate (white spheres), the particle which is sputtered (shaded sphere), and the bombarding particle (black sphere). The interatomic distances are marked in Å. The electronic structure of the model is shown in the inset with electrons depicted by black dots. I is the ionization energy of the sputtered particle and is assumed to be 5.25 eV in this case. φ marked the highest density of the empty electronic states.

The substrate atoms have two electron energy levels separated by 2 eV, the deeper one being 6 eV below the zero (vacuum) level. The bombarding atom has no energy level (simulation of an inert gas ion) and the sputtered atom has only one level, separated by the energy ϵ_a from the vacuum level. The absolute value of ϵ_a, equivalent to the ionization energy I, has been varied to simulate different ionization energies of different sputtered particles. The electron transfer integrals between energy levels of two atoms are assumed to depend on the interatomic distance r_{ij} as $V_{ij}{}^0\exp[\gamma_{ij}(r_{ij}{}^0-r_{ij})]$, where $r_{ij}{}^0$ is equal to 3.36 Å and $V_{ij}{}^0$ to 0.29 eV. The energy levels of the cluster before the impact of the bombarding ion are shown in Fig. 1 in the inset. Also shown is the occupation by six electrons (we neglect the spin degeneracy).

By a proper choice of the impact point, far enough from the sputtered particle to avoid simple binary collision, the kinetic energy E_s of the sputtered particle can be varied from almost zero to energies greater than 100 eV. Using this method of changing E_s, we have calculated the values of R^+ for different E_s keeping $V_{ij}^0 = 0.29$ eV and $\gamma = 1.5$ Å^{-1} the same for all atomic pairs. The resulting dependencies of R^+ on E_s for various ionization energies $I = -\epsilon_a$ are shown in Fig. 2. To demonstrate the dependence of R^+ on the ionization energy I, we plotted in Fig. 3 the values of R^+ (at the fixed kinetic energy of $E_s = 40$ eV) as a function of I in a semilogarithmic plot. The data can be very well interpolated in a wide range of I by a straight line (the full line in Fig. 3). The line corresponds to the exponential dependence $\exp[-(I-\varphi)/kT_e]$ where $T_e = 1800$ °K and $\varphi = 4.1$ eV. Inspecting the inset in Fig. 1, one can see that the value of φ falls just inside the group of the empty cluster levels.

In the next step we have changed various parameters of the cluster and studied the corresponding changes of R^+.

We denote by γ_a the parameter γ between the substrate and the sputtered atom and by γ_s the parameter γ between the substrate atoms. Besides the case mentioned above ($\gamma_a = \gamma_s = 1.5$) we have analyzed and plotted in Fig. 3, further cases: (a) $\gamma_a = 1.5$, $\gamma_s = 3$ (interpolated by dotted lines); (b) $\gamma_a = 3$, $\gamma_s = 1.5$ (dashed-dotted line); (c) $\gamma_a = 3$, $\gamma_s = 3$ (dashed line) (γ in Å^{-1}). The values of V_{ij}^0 are kept equal to 0.29 eV. The calculated results for these faster ionization processes are more scattered than those for the $\gamma_a = \gamma_s = 1.5$ case. Nevertheless, they still can be well interpolated in a reasonable range of I by straight lines and the effective temperatures can be estimated (see Fig. 3).

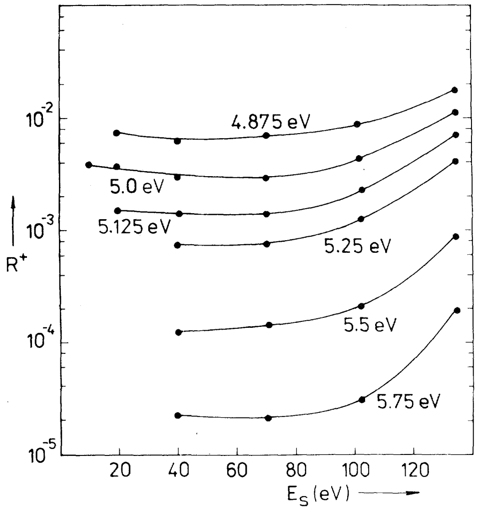

FIG. 2. The calculated ionization yield R^+ as a function of the kinetic energy E_s of the sputtered particle. The parameter is the ionization energy I. The calculation was carried out for $\gamma_a = \gamma_s = 1.5$ Å^{-1}.

In conclusion, we summarize the results of our studies as follows:

(1) The ionization of particles sputtered from an atomic cluster can be very well described by an exponential form $R^+ = \exp[-(I-\varphi)/kT_e]$ in a large range of $I-\varphi$. This is to our knowledge the first time that the functional Boltzmann-like dependence has been established for such rapid, nonstationary processes in systems consisting of only few atoms. The value of φ coincides in our case with the energy at which the empty states of the substrate have the largest density.

(2) The parameter T_e is larger for larger kinetic energies E_s of the sputtered atom. The increase of T_e with increasing E_s can be seen by inspection of the graph in Fig. 2.

(3) The parameter T_e depends upon the spatial

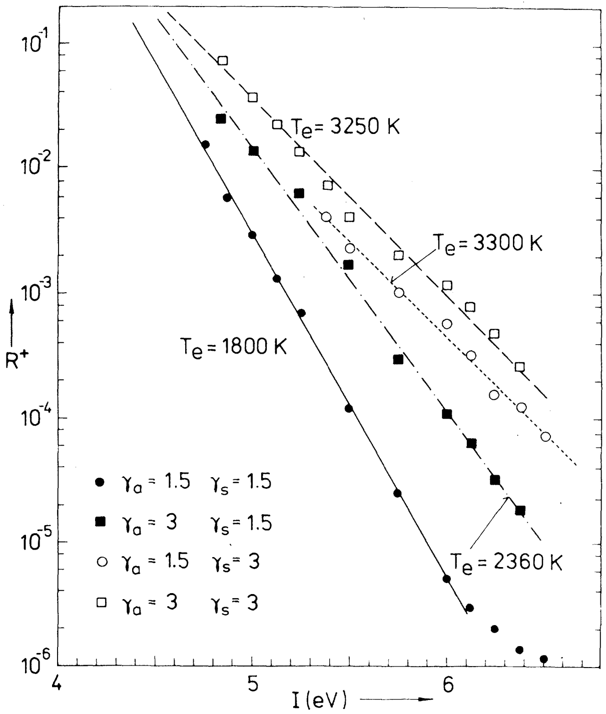

FIG. 3. The calculated ionization yield R^+ as a function of the ionization energy I for various combinations of γ (in inverse angstroms). The data are interpolated by straight lines corresponding to different effective temperatures T_e.

dependence of the transfer integral V_{ij}. The spatial dependence is characterized by γ_{ij} in our study. As seen in Fig. 3, the value of T_e depends not only upon γ between the substrate and the sputtered atom (γ_a) but rather strongly also upon γ between the substrate atoms themselves (γ_s).

(4) The time interval within which the studied process of ionization occurs is found to be 4×10^{-14} sec for $\gamma_a = 1.5$ Å^{-1} and about 2×10^{-14} sec for $\gamma_a = 3$ Å^{-1}. The ionization in a real system involves energy exchange and, hence, energy drain to the colder lattice in this time interval. In view of our limited knowledge of the electronic structure in the collision cascade,[8] it is difficult, at present, to determine reliably the speed with which electronic excitations spread in the cascade region. If one assumes that this region resembles, in the short time interval, a highly disordered solid the excitations may spread by a hopping process and travel in the time τ the distance d given by

$$d = (l v_e \tau)^{1/2}, \tag{5}$$

where l is the length of the hop and v_e is the electron velocity. The distance d clearly depends sensitively upon the electronic structure of the substrate, being smaller for heterogenous materials like oxides and larger for clean metals. For the electronic bandwidth of 3 eV, l equal to the interatomic distance 3 Å, and $\tau = 2\times10^{-14}$ sec, one gets from (5) the value of d equal to 10 Å. This length is not far from the dimension of our model and hence, the outlined conclusions are likely to be valid also in real semi-infinite systems. The LTE should thus be understood in many experimental situations as being local on the atomic scale, i.e., the parameters T_e and φ depend sensitively through the values of γ on the electronic structure of the sputtered atom and its immediate atomic surrounding.

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Zero-Field Spin Relaxation of μ^+ as a Probe of the Spin Dynamics of *Au*Fe and *Cu*Mn Spin-Glasses

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(Received 26 December 1979; revised manuscript received 16 June 1980)

The zero-field spin relaxation of positive muon is measured in spin-glasses *Au*Fe and *Cu*Mn. A stochastic theory of muon spin relaxation in a random dilute spin system is formulated to deduce the correlation time of Fe (or Mn) moments. The observed correlation time increases rapidly from 10^{-10} sec (at $T \sim 1.2T_g$) to 10^{-5} sec (at $T \sim 0.5T_g$), showing a sharp slowing down of spin fluctuation around T_g.

PACS numbers: 76.60.Es

In this paper, we report on the first attempt to measure the dynamical spin fluctuation of spin-glasses *Au*Fe and *Cu*Mn by the zero-field spin relaxation of positive muon (μ^+).[1] Longitudinal spin-relaxation function $G_z(t)$ of μ^+ can be directly obtained by the time-differential measurement of the forward/backward decay positrons emitted from μ^+ stopped in a specimen. This technique[2] allows us to observe the muon-spin relaxation with and without external magnetic field, and