# Ionization of sputtered atoms by resonant laser light near a surface

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A model is proposed for the ionization of a sputtered atom as it interacts with the electromagnetic field of laser light and with a metal surface. This model can be used to study the kinetics of the production of ions and the frequency of selectivity of this production. The increase in the ionization probability is of a resonant nature.

When a solid surface is sputtered by ion bombardment, the production of secondary ions depends on the energy of the primary ions, the electronic structure of the surface, that of the sputtered atom, and the velocity of this atom.[1,2] It has been suggested that mechanism by which a sputtered particle interacting with a surface and an

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electromagnetic field goes into a charged state can be described by the time-dependent Andersen model.[3,4] The Hamiltonian of the system can be written as follows in second-quantization form:

$$H = E_1c_1^+c_1 + E_2c_2^+c_2 + \sum_k E_kc_k^+c_k + \sum_k\sum_j(V_{jk}c_j^+c_k + \text{H.a.}) + (V_{12}c_1^+c_2 + \text{H.a.}).$$

Here $E_k$ is the energy of level $k$ of the metal, and $E_1$ and $E_2$ are the energy levels of the atom which has left the metal surface. The tunneling matrix element $V_{jk}$ depends on the time because the atom is moving away from the surface at a velocity $v_p$ and also because the electrogmagnetic field periodically changes the height of the potential barrier between the atom and the surface: $V_{jk}(t) = V_{jk}^0\exp(-\frac{1}{2}\gamma v_p t)\exp(-S_\sim)$, where $\chi = 2$ Å$^{-1}$, $S_\sim = (1/h)\int_0^{x_{cr}}[m\delta U dx/\sqrt{2m(U_0 - E_j)}]$. $U = U_0 + \delta U$, and $\delta U = eE_\text{L}x\cos(w_\text{L}t)$. Here $\delta U \ll U_0$. Working in the standard way,[2] we transform the equation $i\dot{c} = Hc$ into the system of differential equation

$$i\dot{c}_1 = E_1c_1 + V_{12}c_2 + \sum_k V_{1k}c_k\ ,$$

$$i\dot{c}_2 = V_{21}c_1 + E_2c_2 + \sum_k V_{2k}c_k\ ,$$

$$i\dot{c}_k = V_{k1}c_1 + V_{k2}c_2 + \sum_k E_kc_k.$$

This system can be written in the matrix form $i\dot{C} = -WC$, where $C = \begin{pmatrix} c_1 \\ c_2 \\ c_K \end{pmatrix}$. By diagonalizing this matrix under the assumption $V_{ij} = V_{ji}$, $i,j = 1,2,k$, we can find its diagonal term $W_{22}$. A solution of the equation, $c_2$, is found in the following way: $c_2 = c_{02}\exp(-i\int W_{22}dt)$. Using this solution, we can find the quantity $\langle n_2(t)\rangle = \langle c_2^+(t)c_2(t)\rangle$. The expression for $\langle n_2(t)\rangle$ is as follows under the conditions $\hbar w_{12} \ll E_1, E_2$ and $\Delta_{1k} \ll \Delta_{12}$, $\Delta_{2k}$: $\langle n_2(t)\rangle \simeq n_{02}\exp(-\int\alpha(t)dt)$. Here $\alpha(t) = \Delta_{12}(t) + \Delta_{2k}(t)$, $n_{02}$ is a constant, and $\Delta_{ij} = \pi\Sigma_k V_{kj}V_{ik}\delta(w - E_k/h)$.

Here are the kinetic equations for the level populations of the sputtered atom:[5]

$$\dot{n}_1 = -\Delta_{12}(n_1 - n_2)\ ,$$

$$\dot{n}_2 = -\left(\frac{2\Delta_{2k}}{\hbar}\right)(1 - f(E_2(t), T_e))n_2 + \Delta_{12}(n_1 - n_2),$$

where $f(E_2(t), T_e)$ is the Fermi-Dirac function. We assume that the electrons have an equilibrium distribution. Solving the system for $n_2(t)$, we obtain

$$n_2(t) = \frac{n_0\Delta_{12}}{B_2 - B_1}(e^{B_1t} - e^{B_2t}),$$

where $B_{1,2} = (\Delta_{12} - \frac{1}{2}\Delta_{2k}) \pm \sqrt{\Delta_{12}^2 \cdot \frac{1}{4}(1 - \Delta_{2k}/2\Delta_{12}) + \Delta_{12}\Delta_{2k}}$.

The width of a level at time $t$ during the withdrawal from the surface, as the height of the potential barrier varies periodically, is given by

$$\Delta_{2k}(t) = \Delta_0 \exp(-\gamma v_p t) \cdot \exp\left(-\frac{2}{h}\int_0^{x_{cr}} \frac{m\delta U\, dx}{\sqrt{2m(U_0 - E_2)}}\right).$$

If the frequency at which the barrier height oscillates is lower than the rate at which an electron collides with the barrier wall, the tunneling probability can be averaged over the oscillation period:

$$< \Delta_{2k}(t) >= \Delta_0\, w_L \int_0^{1/w_L} e^{-\gamma v_p t} \cdot e^{z\cos(w_L t)}\, dt,$$

where $z = meE_2 x_{cr}^2 / h\sqrt{2m(U_0 - E_2)}$. An estimate of the average transmission of the potential barrier reveals that the probability for resonant tunneling increases by four orders of magnitude. In this case the condition for the occurrence of resonant tunneling is $E_2(t) > E_F$, or, in terms of the critical distance from the surface, $x_{cr} < (1/\gamma)\ln\{[E_2(\infty) - E_2(0)]/[E_2(\infty) - E_F]\}$. The ionization probability in this case is $P^+ \sim 0.1$. This estimate is higher than the estimated probability for an ionization due exclusively to ion sputtering:[6] $P^+ \sim 0.01$–$0.001$.

If the frequency ($\delta$) at which the population of the excited level oscillates is close to the frequency ($w_L$) at which the height of the potential barrier oscillates, a resonant ionization regime will arise. In this regime, all excited atoms are ionized as the result of a resonant tunneling of electrons from the excited level into the metal. In this case the ionization probability is

$$P^+(t) \simeq P_0 e^{-ht} \cdot e^{z\cos(w_L t)}(1 - \cos(\delta t)),$$

where $h = \gamma v_p$, $\delta = \sqrt{\delta_0^2 + \Omega_R^2}$, $\delta_0 = w_L - w_{12}$, and $\Omega_R$ is the Rabi frequency. The first factor here is a measure of the decrease in the ionization probability as the atom moves away from the metal surface at a velocity $v_p$. The second and third factors describe the oscillations in the ionization probability due to the periodic change in the

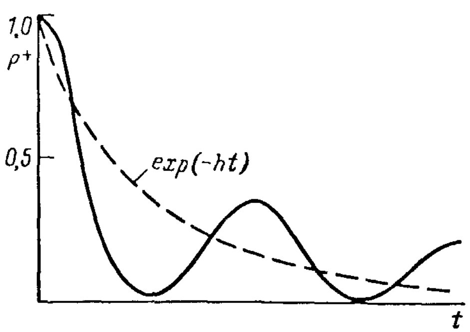


FIG. 1. Probability for the ionization of a sputtered atom near a surface as a function of the time under the conditions $h < w_L$, $\delta$.

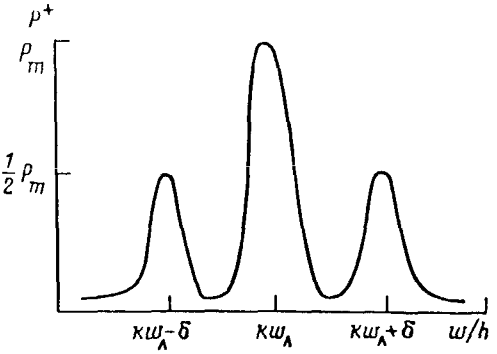


FIG. 2. "Lorentzian" spectra of the probability for the ionization of an atom near a surface ($\sigma^2 - \pi P_m h$).

barrier height and the oscillations in the population of the excited level. As the sputtered atoms move away from the surface, the yield of secondary ions represents an integral over the atomic ionization processes at a certain laser frequency. Figures 1 and 2 show the probability for the ionization of sputtered atoms as a function of (in Fig. 1) the time which has elapsed during the motion away from the surface and (in Fig. 2) the light frequency. The width of the peaks on the spectral characteristic is determined by $\sigma^2$. The dependence of the ionization probability on the light intensity, $P^+ \sim \exp(\sqrt{I})$, differs from the results of Ref. 4 because of the coherent preparation of the barrier.

At laser light intensities 1–10 $kW/cm^2$, the number of particles which are evaporated during one pulse ($\tau_{pulse} \sim 10$ ns) is $10^6$–$10^7$ (the evaporation results from photodesorption; the quantum efficiency of the process is[7] $10^{-7}$). This is fewer than the number of particles which are sputtered by ion bombardment (this number would be $N \sim 10^8$ atoms at an ion current $I_{Ar}$ of 1 mA, at an ion energy of 5 keV, and at a sputtering coefficient $s \sim 1$). It was observed in Ref. 8 that the average value of the secondary-ion current of the current pulses of the secondary-ion emission is greater in amplitude than the pulses to the average value [*sic*].

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