PHYSICAL REVIEW B VOLUME 54, NUMBER 10 1 SEPTEMBER 1996-II

Effect of the local electronic temperature on secondary-ion spectra

D. V. Klushin, M. Yu. Gusev, S. A. Lysenko, and I. F. Urazgil'din
Department of Physics, Moscow State University, Moscow 119899, Russia

(Received 27 November 1995)

The problem of secondary-ion formation is investigated theoretically and experimentally. The effect of local electronic temperature on the collisional cascade region in the secondary-ion energy spectrum is examined. It is shown that the shift of the maximum of the energy spectrum with a change of the emission angle is explained well under the assumption of local heating of the electronic subsystem followed by cooling down. [S0163-1829(96)04133-1]

I. INTRODUCTION

Electron exchange between an atomic particle and a solid surface in secondary-ion emission has been the field of interest of many experimental and theoretical groups during the last years. In spite of this attention and importance, the mechanism of secondary-ion formation is still poorly understood (see, for example, the review of Yu[1]).

In this paper we study the effect of the local electronic temperature on the energy spectra of secondary ions. Experimentally, these spectra are shifted with increasing emission angle, usually towards higher energies. So far, attempts to explain this effect have used the electron-tunneling model to describe charge-state formation of a secondary particle.[2–5] The model allowed one to describe the experimental shapes of the energy spectra, but led to a overestimation of the absolute values of the ionization probability by several orders of magnitude.[6] Below we demonstrate that the local heating of the electronic subsystem in the collisional cascade area and its subsequent cooling down (in particular, during charge-state formation) should be taken into account for an adequate description of the experimental observations.

II. IONIZATION PROBABILITY OF ATOMIC PARTICLES SPUTTERED FROM METALS

The energy distribution of secondary ions depends on the processes of charge exchange during secondary-ion emission. In this section we will consider the mechanisms responsible for the formation of the charge state of the escaping atomic particle.

Two theoretical models of electron exchange in secondary-ion emission are most widely used: the electron-tunneling model[2–5] and the substrate-excitation model of Sroubek.[7]

In Ref. 8 two charge-state formation mechanisms were shown to operate simultaneously, namely, the tunneling and thermalization mechanisms, which can be related to the two above-mentioned models. The theory gives a quantitative description of the experimental data using the local electronic temperature as a fitting parameter. The obtained theoretical results do not disagree with either the electron-tunneling model or the one by Sroubek. Moreover, under certain conditions either of these models becomes a particular case of the proposed theory, which can be considered as a unification of the previous models (see Fig. 1). The ionization probability P^+ of a secondary particle can be presented as:[8]

$$P^+ = \exp\left[-\frac{2\Delta(z_0)}{\gamma v_\perp}\right] + \Gamma\left(\frac{|E_a'(z^*)|}{\gamma T_e}+1\right) \times \exp\left[-\frac{|E_a(z^*)|}{T_e}\right], \tag{1}$$

where $v_\perp$ is the normal component of the secondary-particle velocity; T_e is the local electronic temperature; $E_a(z)$ is the valence level of an atomic particle, $E_a'(z)=\partial(E_a(z))/\partial z$; z is distance from the surface; $\Delta(z)$ is the half-width of the level, $\Delta(z)=\Delta_0\exp[-\gamma z]$, where γ is the inverse of the characteristic length related to the electronic wave function; z_0 is the effective distance of neutralization; z^* is the effective thermalization distance $[z^*=\gamma^{-1}\ln(2\Delta_0/\gamma v_\perp)]$; and Γ is the gamma function.

The first term in the expression (1) for the ionization probability P^+ results mostly from kinetic effects induced by the rapid change of $E_a(z)$ with z when it crosses the Fermi level. The second term represents the ''thermalization'' of

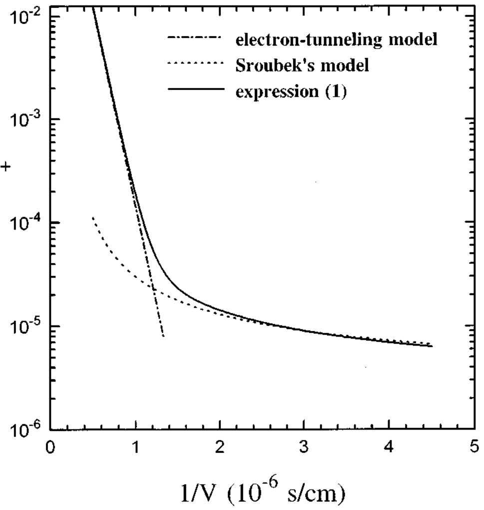

FIG. 1. Typical dependence of the ionization probability of secondary particles on the inverse velocity.

0163-1829/96/54(10)/7062(5)/$10.00

the atomic level, i.e., the tendency towards equilibrium occupation corresponding to the local electronic temperature T_e.

The problem of the electronic temperature in the cascade region is now under discussion. This temperature can be expected to differ significantly from the ionic one and be as large as few thousands of K.[9] The ionization probability and, as a consequence, the energy spectra depend on the local electronic temperature, which varies in time.

III. TIME DEPENDENCE OF THE ELECTRONIC TEMPERATURE IN A COLLISION CASCADE

Secondary-ion emission normally occurs as a result of a collision cascade in the solid. A fraction of the energy of the cascade is transferred to the electronic subsystem.

The effect of the collision cascade on the electronic subsystem can be represented by an effective heat source $Q(r,t)$ (see Ref. 10):

$$Q(r,t)=Q_0F(r,t), \tag{2}$$

where Q_0 is the power of the source (during the bombardment of surface with atomic particles of keV energies, $Q_0 \sim 0.1–1$ eV/fs), and $F(r,t)$ gives the distribution of the source in space and time [$F(r,t)$ is normalized to the cascade volume].

Since we are mainly interested in the time dependence of the electronic temperature, we choose a convenient spatial shape of $F(r,t)$ and focus on the peculiarities of the time dependence of the source:

$$F(r,t)=\frac{\exp[-r^2/r_0^2(t)]}{\pi^{3/2}r_0^3(t)}\,f(t), \tag{3}$$

where the cascade center is taken to be the coordinate origin. The function $r_0(t)$ describes the current size of the cascade, and the function $f(t)$ is related to the processes of cascade development and decay ($\max[f(t)]=1$).

Approximately after 100 fs, the number of atomic particles knocked out from their equilibrium positions no longer increases.[11] It can therefore be said that the formation of a cascade region (with size of about $r_0 \sim 20$ Å) is over. This is approximately the time when the emission of secondary atomic particles with energies near the spectrum maximum is started. Then the cascade decays; i.e., the atomic subsystem returns to the equilibrium configuration. The characteristic time for this process, which is on the order of several hundreds of fs ($\sim$500–1000 fs),[11] determines the time scale for $f(t)$. In the time interval of charge-state formation (between 100 and 300 fs after the primary-ion impact), $f(t)$ is a decreasing function $[f(t)\sim 1]$.

If the electron subsystem is in a local quasiequilibrium, we can speak about a local electronic temperature. This is correct only in the case when the characteristic time scale connected with the time scale of the heat source (several 100 fs) is larger than the time of the local quasithermalization of the electron subsystem. As appears from the time-resolved photoelectron spectroscopy data (see Ref. 12), this condition seems to be valid especially at an enhanced temperature. Of course, a small fraction of nonthermalized electrons is present in electron distribution (see Ref. 13). But for the charge-state formation process, small deviations from the Fermi-Dirac distribution with a local enhanced temperature are not important. Therefore, we can use the heat conduction equation for the electron subsystem:

$$C_e\partial T_e/\partial t+\nabla\vec{q}=Q(r,t)-g(T_e-T_f), \tag{4}$$

where C_e is electronic heat capacity per unit volume. For a degenerate Fermi system, $C_e=\alpha T_e$, where $\alpha=\pi^2\nu_F/3$, ν_F is the density of electron states at the Fermi surface; $\vec{q}$ is the vector of heat flux, $\vec{q}=-\kappa_e\nabla T_e$, and κ_e is the thermal conductivity of electrons. For a degenerate Fermi system, $\kappa_e=\alpha D_eT_e$, where D_e is the electron diffusion coefficient (in the cascade region, $D_e\sim 10$ Å^2/fs; see Ref. 14).

The second term on the right-hand side of Eq. (4) describes the energy loss from electrons to the phonon subsystem; g is the constant of the electron-phonon interaction, and T_f is the temperature of the phonon subsystem. The constant g is of about $10^{16}–10^{17}$ W/m^3 K.[13] In the cascade region in the time interval of interest (between 100 and 300 fs after the keV primary-ion energy impact), this term will be very small compared to the one describing the energy supply to the electron subsystem from the moving atoms [i.e., $Q_0/\pi^{3/2}r_0^3(t)\gg gT_e$, even for $T_e\sim 1$ eV] and can be neglected. The effect of phonon creation on the electronic temperature can be important at some distance from the heat source (the collision cascade zone) and also after the source becomes weak. But as we are interested in the situation in the cascade region at the time when the cascade is active, energy transfer from electrons to phonons can be disregarded.

It is convenient to rewrite Eq. (4) for a function $u(r,t)$ which is given by the equation

$$T_e^2=T_0^2+u(r,t), \tag{5}$$

where T_0 is the bulk temperature.

We arrive at a nonuniform diffusion equation with zero initial conditions:

$$\partial u(r,t)/\partial t=D_e\nabla^2u(r,t)+2Q(r,t)/\alpha,$$

$$u(r,t=0)=0. \tag{6}$$

The solution is

$$u(r,t)=\frac{2}{\alpha}\int_0^t d\tau\int_{-\infty}^{+\infty}d^3r'\;G(r,r',t-\tau)Q(r',\tau),$$

$$G(r,r',t-\tau)=[4\pi D_e(t-\tau)]^{-3/2}\exp\left[-\frac{|\vec{r}-\vec{r}'|^2}{4D_e(t-\tau)}\right]. \tag{7}$$

Now we take into account the fact that

$$[\partial f/\partial t][r_0^2/4D_e]\ll f,$$

$$[\partial r_0/\partial t][r_0^2/4D_e]\ll r_0, \tag{8}$$

where $r_0^2/4D_e\sim 10$ fs when the cascade radius $r_0\sim 20$ Å.

The inequalities (8) seem to be quite reasonable since the time behavior of $f(t)$ and $r_o(t)$ is governed by atomic collisions, whose time scale is larger than $r_0^2/4D_e$.

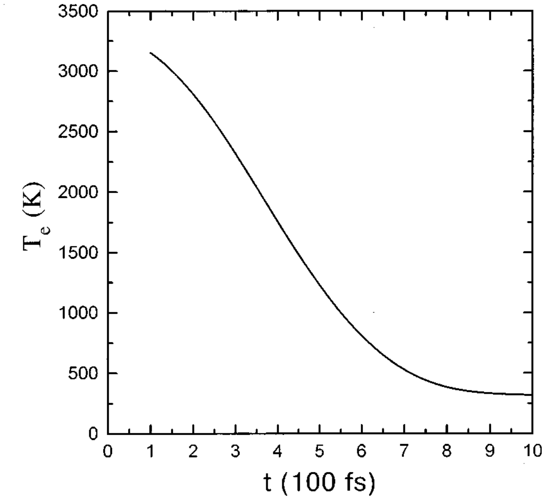

FIG. 2. Cooling down of the electron subsystem in the cascade region.

Taking relations (8) into account, the solution for $u(r,t)$ inside the cascade region [i.e., at $r<r_0(t)$] becomes

$$u(r,t)=\frac{Q_0 f(t)}{2\alpha D_e r_0(t)}\,\frac{r_0(t)}{r}\,\mathrm{erf}\left(\frac{r}{r_0(t)}\right), \tag{9}$$

where erf(x) is the error function integral; erf(x)/$x\sim1$ at $x<1$.

Therefore, the time dependence of the electronic temperature $T_e(t)$ in the cascade is given by

$$T_e=\left[T_0^2+\frac{Q_0 f(t)}{2\alpha D_e r_0(t)}\right]^{1/2}. \tag{10}$$

We assume the sample to be at room temperature $T_0\sim300$ K. In the case of the bombardment of a metal surface with keV atomic particles, knowing the cascade characteristics $Q_0\sim0.1$–1 eV/fs, $D_e\sim10$ Å^2/fs, $r_0\sim20$ Å and taking into account that $\alpha\sim50$ J/m^3 K^2, the parameter $Q_0/2\alpha D_e r_0$ can be found to be on the order of 10^6–10^7 K^2. Therefore, local heating of the electron subsystem by up to several thousand K is possible.

We recall that the cascade expands most rapidly during the first 100 fs (cascade lifetime is on the order of 500–1000 fs). The emission of the majority of the secondary particles begins approximately 100–200 fs after the start of the cascade. The heating of the electron subsystem takes place at the initial stage of the cascade development, while the emission of the secondary particles with energies near the maximum of the energy distribution occurs at the stage of the cooling down of the electron subsystem. Therefore, for $t>100$ fs the dependences $f(t)$ and $r_0(t)$ were modeled as follows: $f(t)=\exp[-(t-100\text{ fs})^2/(500\text{ fs})^2]$ and $r_0(t)=5$ Å$+15$ Å$\times(1-\exp[-t/100\text{ fs}])$. The time dependence of the electronic temperature in the cascade region $T_e(t)$ is given in Fig. 2.

The smaller the normal component of the secondary-particle velocity, the larger the time of the secondary-ion formation, and the greater the variation of the electronic temperature during the charge exchange. Thus, in the case of a low-energy secondary particle or large emission angle, the cooling of the electronic subsystem can be especially important.

IV. VALIDITY OF THE THEORY FOR SEMICONDUCTORS

So far, we have been considering metals where the energy for excitation of electrons near the Fermi surface can be infinitely small. It could be expected that in semiconductors, the presence of a band gap should render the above theory inapplicable. However, some recent results (e.g., Ref. 14) indicate the metallization of the semiconductor in the cascade region. In Ref. 14, the density of electronic states in silicon in the cascade area is calculated and found to be metal-like and similar to that of aluminum.

V. INFLUENCE OF ELECTRON SUBSYSTEM COOLING ON CHARGE EXCHANGE

As was mentioned in Sec. III, in the case of a small energy of the secondary particle, the cooling of the electronic subsystem becomes important in the processes of charge-state formation. Rigorous treatment of this effect in the framework of quantum theory is a difficult problem because the temperature is not a dynamical variable. However, in the thermally dominated case we can use the so-called ''probability approach'',[15] in which one writes down a master equation for the probability of the occupation of the atomic level $\langle n_a(t)\rangle$,

$$d\langle n_a(t)\rangle/dt=2\Delta(z)[F_F(E_a(z),T_e(t))-\langle n_a(t)\rangle], \tag{11}$$

where the terms on the right-hand side are the tunneling probability to and from the atom [note that $\Delta(z)$ is the level half-width; F_F is the Fermi distribution with the electronic temperature]. Within the probability approach, we can consider the electronic temperature as a known time-dependent function $T_e(t)$. In this case we obtain the same formula (1) for the ionization probability in which the electronic temperature T_e=const is replaced by the value $T_e(t^*)$, where $t^*=z^*/v_\perp$. When the thermalization mechanism plays the major role, the second term in formula (1) predominates and we have

$$P^+\approx\exp\left[-\frac{|E_a(z^*)|}{T_e(t^*)}\right]. \tag{12}$$

Thus we have established a dependence between T_e and the normal component of the secondary-particle velocity through the parameter $t^*=z^*/v_\perp$. This is only natural because the slower the escaping particle, the lower the effective electronic temperature.

VI. FORMATION OF THE ENERGY SPECTRA OF SECONDARY IONS

The energy and angular distribution of secondary ions $S^+(E,\theta)$ (E is the energy of the escaping particle, and the angle θ is counted off from the surface normal) is determined by the respective distribution of all the atomic particles emitted, $S(E,\theta)$, and the ionization probability $P^+(E,\theta)$, i.e.,

$$S^{+}(E,\theta)=S(E,\theta)P^{+}(E,\theta). \tag{13}$$

The $S(E,\theta)$ distribution is most often described by the expression which follows from Sigmund's cascade theory:[16]

$$S(E,\theta)\sim\frac{E\ \cos\theta}{(E+U)^{3}}, \tag{14}$$

where U is the binding energy of a surface atom.

For the secondary-ion energy near the energy maximum (5–15 eV) and an exit angle range covered in experiments (0°–70°), the thermalization mechanism predominates.[8] Therefore, we can use formula (12) for the ionization probability.

From the formula for $T_e(t)$ derived in Sec. III, in the case $T_e \gg T_0$, we have $T_e\sim\sqrt{f(t)}$, where $f(t)\sim\exp[-t^2/t_0^2]$; t is counted from the start of emission, and the constant t_0 is related to the lifetime of the collision cascade. Then, $T_e(t^*)=T_{0e}\exp[-t^{*2}/2t_0^2]=T_{0e}\exp[-z^{*2}/2v_\perp^2 t_0^2]$. The parameter T_{0e} can be estimated from the absolute value of the ionization probability. Normally, T_{0e} is on the order of several thousand K (e.g., for Si, $T_{0e}\sim3000$ K).

The position of the maximum of the energy spectrum, $E_{\max}(\theta)$, can be found from the condition $\partial S^{+}/\partial E=0$, which leads to the equation

$$E=\frac{U}{2}\left(1+\frac{3f(E,\theta)}{2-f(E,\theta)}\right),$$

$$f(E,\theta)=-\frac{E_a(z^*)}{T_e}\frac{t^{*2}[1+(\gamma z^*)^{-1}]}{2t_0^2}-\frac{E_a'(z^*)}{2\gamma T_e}. \tag{15}$$

Equation (15) can be solved numerically to give the required $E_{\max}(\theta)$ dependence. The parameters γ, $E_a(z)$, and $\Delta(z)$ are system dependent and can be calculated in every particular case (see, for example, Ref. 8). The binding energy U can be found from the energy spectrum of the sputtered atoms, whose maximum corresponds to $U/2$ (for Si, $U\sim4.2$ eV).

Analysis of the function $E_{\max}(\theta)$ (see Fig. 3) shows that even a slight cooling of the electronic subsystem on a time scale of charge-state formation (~100 fs) can significantly affect the energy spectrum of secondary ions, especially at large emission angles.

VII. COMPARISON WITH THE EXPERIMENTAL DATA

Secondary-ion emission from the (111) face of Si single crystals of *n* and *p* type was studied with energy and angular resolution and for various incident angles. Boron-doped ($n=10^{18}$ cm^{-3}) and phosphorus-doped ($n=10^{14}$ cm^{-3}) samples were chosen for the investigation. The samples were bombarded with 6-keV Ar^{+} ions. The angles of incidence, ψ, were 5° and 20° and the angle of observation, θ, varied from 35° to 65° (the angles are measured from the surface normal). With increasing θ, the shape of the energy spectra change and the positions of the maxima are shifted towards larger energies. Both samples show the same results, and this fact is in favor of the metallization of the semiconductor in the cascade region. The positions of maxima of energy spectra did not change with increasing ψ.

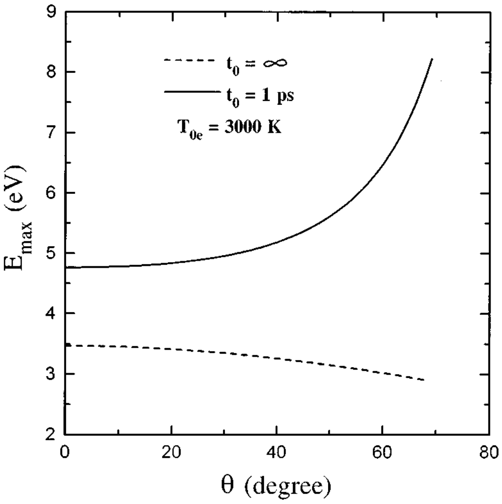

FIG. 3. Position of the energy spectrum maximum of secondary ions as a function of the emission angle with (t_0=1 ps) and without ($t_0=\infty$) taking into account the cooling down of the electron subsystem. The parameters are as follows: U=4.2 eV, Δ_0=2 eV, γ=1 Å^{-1}, $E_a(z)$ (in a.u.)$=E_a^0+1/4(z-z_{im})$, $E_a^0=-4$ eV, and z_{im}=0.5 Å.

Figure 4 presents the experimental and calculated dependences of the position of the energy spectrum maximum on the emission angle. The shapes of the energy spectra and their angular dependence for the Si samples studied are in agreement with theoretical calculations, as illustrated in Fig. 4. In the calculation, the cascade lifetime was $t_0\sim500$ fs in agreement with the estimates in Ref. 11. It is important to note that the calculated ionization probability $P^{+}\sim10^{-4}$–10^{-5} agrees well with the experimental values. Therefore, the proposed theory adequately describes both the ionization probability and the angular behavior of the secondary-ion energy spectrum.

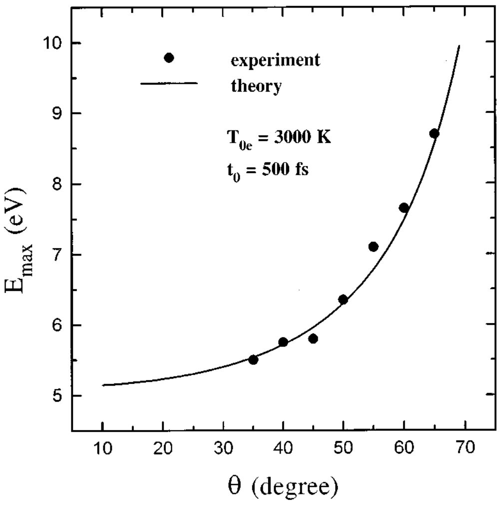

FIG. 4. Position of the energy spectrum maximum of secondary ions of Si^{+} as a function of the emission angle. The cascade lifetime is $t_0\sim500$ fs. The parameters U, γ, Δ_0, and E_a are the same as in Fig. 3.

VIII. CONCLUSION

In conclusion, the effect of the local electronic temperature in the cascade region on secondary-ion formation has been considered. The time dependence of the electronic temperature was examined. It is shown that the time dependence of the electronic temperature affects the energy spectra of secondary ions. The shift of the maximum $E_{\max}(\theta)$ of the energy spectrum of secondary ions towards higher energies with increasing of the emission angle is explained well under the assumption of local heating of the electronic subsystem followed by its cooling down. There is good agreement between the experimental and calculated results for both $E_{\max}(\theta)$ and for the order of magnitude of ionization probability of the secondary particle.

ACKNOWLEDGMENTS

This work was supported in part by the International Science Foundation (Grant No. MQ 1300) and the Russian Foundation for Basic Research (Grant No. 96-02-17744 A).

---

[1] M. L. Yu, in *Sputtering by Particle Bombardment III*, edited by by R. Behrish and K. Wittmaack, Springer Series in Topics in Applied Physics Vol. 64 (Springer, Berlin, 1991), p. 91.

[2] A. Blandin, A. Nourtier, and D. W. Hone, J. Phys. (Paris) **37**, 369 (1976).

[3] J. K. Norskov and B. I. Lundqvist, Phys. Rev. B **19**, 5661 (1979).

[4] R. Brako and D. M. Newns, Surf. Sci. **108**, 253 (1981).

[5] N. D. Lang, Phys. Rev. B **27**, 2019 (1983).

[6] I. F. Urazgildin, Nucl. Instrum. Methods B **78**, 271 (1993).

[7] Z. Sroubek, Phys. Rev. B **25**, 6046 (1982); Nucl. Instrum. Methods Phys. Res. **194**, 533 (1982).

[8] D. V. Klushin, M. Yu. Gusev, and I. F. Urazgildin, Nucl. Instrum. Methods B **100**, 316 (1995).

[9] Z. Sroubek and G. Falcone, Surf. Sci. **166**, L136 (1986); Z. Sroubek, Appl. Phys. Lett. **45**, 850 (1984).

[10] J. Lindhard and M. Scharff, Phys. Rev. **124**, 128 (1961).

[11] M. W. Thompson, *Defects and Radiation Damage in Metals* (Cambridge University Press, Cambridge, England, 1969), Chap. 5.

[12] J. R. Goldman and J. A. Prybyla, Phys. Rev. Lett. **72**, 1364 (1994).

[13] W. S. Fann, R. Storz, H. W. K. Tom, and J. Bokor, Phys. Rev. Lett. **68**, 2834 (1992).

[14] Z. Sroubek and J. Fine, Nucl. Instrum. Methods B **100**, 253 (1995).

[15] J. J. C. Geerlings, J. Los, J. P. Gauyacq, and N. M. Temme, Surf. Sci. **172**, 257 (1986).

[16] M. W. Thompson, Philos. Mag. **18**, 377 (1968); P. Sigmund, Phys. Rev. **184**, 383 (1969).