

Energy Distribution of Secondary Electrons Emitted from Solid Surfaces under Ion Bombardment

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By considering the excitation of the free electron gas system, we have theoretically investigated the energy distribution of secondary electrons (SE's) emitted from the metal surfaces under ion bombardment. The main quantities in the theory are the energy-dependent inelastic mean free path, the stopping power for excited electrons inside, and the internal SE energy distribution per unit primary path. The internal distribution has been studied especially in detail and is found not to diverge at the Fermi energy because of the dynamical screening effect. This is quite different from the previously used theories. The surface transmission was treated quantum-mechanically. The energy distribution of SE's emitted from Al was calculated and discussed.

1. Introduction

Since the phenomenon of secondary electron (SE) emission was discovered in the beginning of this century, secondary electron emission spectroscopy has been a growing field of spectroscopy which yields information about the chemical composition and electronic state of atoms and the work function at solid surfaces. The energy distribution and the yield of SE have been studied intensively under electron bombardment¹⁾⁻⁸⁾ or ion bombardment. Recently, SE spectroscopy has been utilized to the investigation of the bombardment-induced work function changes during sputter removal of the metal oxide layers⁹⁾.

Theoretically, the energy distribution of the emitted secondary electrons have been considered from three physical processes. Namely, the creation of internal excited SE's by the primary ion beams per primary path (i. e. the source excitation function), the propagation of SE's from their original position to the surface, and the transmission of the surface barrier potential. The problem of electron transport have been treated in terms of the Boltzmann equation^{2),7)}, the continuous slowing down approximation (C-SDA)^{3),5)}, and the escape depth probability¹⁰⁾. Concerning the source excitation

function, the result using a bare Coulomb interaction⁴⁾ has been often used, which diverges at the Fermi level. The transmission problem of the surface potential barrier has been treated classically in most cases. In the escape depth problem, the inelastic mean free path (MFP) $\lambda(E)$ plays a dominant role. In order to estimate $\lambda(E)$, the dielectric function of the Fermi gas has been used widely and successfully¹¹⁾.

This paper treats the energy distribution of secondary electrons which are excited in the Fermi gas and emitted from the solid surface. The theory is developed on a basis of the dielectric response of the media. Throughout the paper, m , e , \hbar , and a_0 denote the electron rest mass, the elementary charge, the Planck constant divided by 2π , and the Bohr radius ($= 2.18 \times 10^8$ cm/s), respectively.

2. Theory.

Here we develop the theory of the energy distribution of secondary electrons (SE's) emitted from solids on the basis of three physical processes mentioned in the introduction. The case is considered where the primary electrons of normal incidence penetrate a solid along a straight line trajectory. Let z denote the position measured from the surface toward the inside surface normal. In addition, θ and ϕ indicates the angles at which the directions of the internal and the external secondaries make with the outside surface normal (see fig. 1). In addition, E_0 , E and E' are the kinetic energies of excited secondaries at a created position, at the surface, and after transmitting the surface. E_p is the kinetic energy of a primary ion. Note that E_0 and E are measured from the bottom of a conduction band, while E' is measured from the vacuum level.

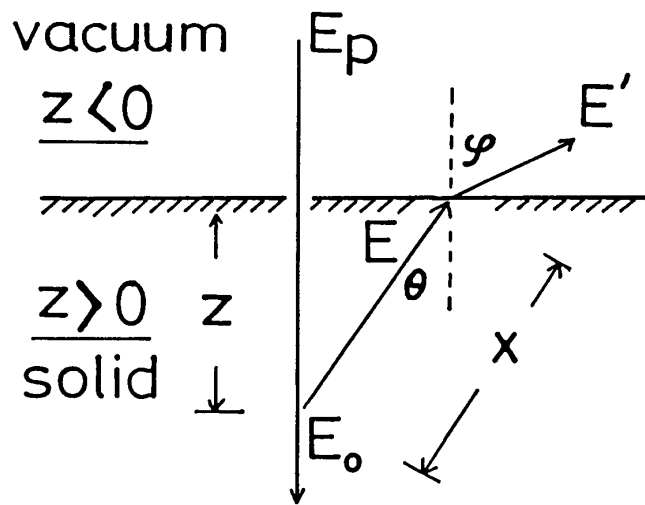


Fig. 1 Schematic diagram illustrating the geometry and the symbols used in the text.

We restrict our attention to the excitation of the free electron gas governed by the Fermi distribution so that the band effect etc. are ignored. In this case, the dielectric function characterizes the system and it is represented only by the r_s value, ranging from 1.5 to 5.8 for typical metals.

2-1 Inelastic MFP and stopping power of excited electrons

According to Quinn and Ferrell¹²⁾, the inverse inelastic mean free path $1/\lambda(E)$ to be of the forms¹¹⁾

$$1/\lambda(E) = \hbar / (\pi a_0 E) \int_0^{(E-E_f)/\hbar} d\omega \int_{k_1(\omega)}^{k_2(\omega)} dk / k \operatorname{Im}\{-1/\epsilon(k, \omega)\}, \quad (1)$$

Similarly, the electronic stopping power of the Fermi gas for penetrating electrons is found to be

$$S(E) = \hbar^2 / (\pi a_0 E) \int_0^{(E-E_f)/\hbar} d\omega \omega \int_{k_1(\omega)}^{k_2(\omega)} dk / k \operatorname{Im}\{-1/\epsilon(k, \omega)\},$$

where the maximum and minimum momentum transfers, $k_2(\omega)$ and $k_1(\omega)$ are given by

$$k_1(\omega) = (2m)^{1/2} \{ E^{1/2} - (E - \hbar\omega)^{1/2} \} / \hbar, \quad (3)$$

$$k_2(\omega) = (2m)^{1/2} \{ E^{1/2} + (E - \hbar\omega)^{1/2} \} / \hbar. \quad (4)$$

In the above equations, $\epsilon(k, \omega)$ is the dielectric function and n_0 is the number density of electrons, relating to the r_s value and the Fermi wave number k_f as follows:

$$4\pi r_s^3 / 3 = 1 / (a_0 n_0), \quad \text{and} \quad k_f = (3\pi^2 n_0)^{1/3}. \quad (5)$$

In figure 2, the calculated $\lambda(E)$ and $S(E)$ values of the electron gas with $r_s = 1.5$ and 3 are plotted against $E - E_f$ with the use of the Lindhard dielectric function¹³⁾. Each curve in the figure has a hump or a dip contributed from the plasmon excitation. In the low energy region, $S(E)$ is nearly proportional to $E^{2.5}$. In the high energy region, $S(E)$ reduce to the Bethe form.

2-2 Internal SE's

Let us consider the excitation of the Fermi gas by the ion beam. We denote by $dn(E_0, E_p, z) / dE_0$ the number of secondaries excited per unit energy into an interval $(E_0, E_0 + dE_0)$ per unit primary path created in a section $(z, z + dz)$ by ions with energy E_p . The ion is assumed to move inside the material along a straight-line

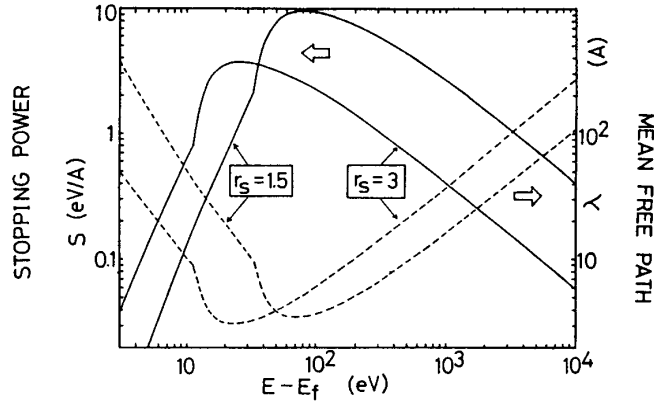


Fig. 2 The inelastic mean free path $\lambda(E)$ (.....) and the stopping power $S(E)$ (———) of the free electron gas with $r_s = 1.5$ and 3.0 for a penetrating electron with kinetic energy E .

trajectory, since its kinetic energy of incidence is high enough. When momentum $\hbar k$ is transferred to the Fermi gas, the center of the occupied momentum sphere, i. e. the Fermi sphere, shifts from the origin by the amount $\hbar k$. Thus the electrons having momentum greater than the Fermi momentum p_f are responsible for the internal secondary electrons. In order to calculate the energy distribution of internal SE's, a parameter μ , defined by p/p_f or $(E_0/E_f)^{1/2}$, is introduced as a measure of kinetic energy E_0 . Here $E_f = (\hbar k_f)^2/2m$. Then for secondaries, we have interest in the range of $\mu > 1$. First let us count the number of electrons per unit volume with momentum greater than μp_f , or, energy greater than $\mu^2 E_f$. Following Baroody³⁾, for a given reduced momentum transfer $s = \hbar k/\hbar k_f$, this quantity is calculated as

$$N(\mu, s) = \pi k_f^3 / \{ 6s(2\pi)^3 \} [3(\mu^2 - 1)^2 - 8s(\mu^3 - 1) + 6s^2(\mu^2 + 1) - s^4], \text{ for } \mu - 1 \leq s < \mu + 1, \quad (6)$$

$$= 8\pi k_f^3 / \{ 3(2\pi)^3 \}, \text{ for } \mu + 1 \leq s. \quad (7)$$

Then, the total number of excited electrons having momentum greater than μp_f per unit primary path, $dn_1(\mu, E_p)/dz$, calculated by integrating $N(\mu, s)$ multiplied by the differential momentum transfer cross section over possible momentum transfers. In the case of ion bombardment, it is expressed as

$$dn_1(\mu, E_p)/dz = \hbar / (\pi a_0 E_p) (1/n_0) \int_0^\infty d\omega \int_{\omega/v}^\infty dk/k \operatorname{Im}\{ -1/\epsilon(k, \omega) \} \\ \times N(\mu, k/k_f). \quad (8)$$

The energy distribution of internal secondaries excited per unit primary path, $d^2n(E_0, E_p)/dE_0 dz$, can be calculated by differentiating $dn_1(\mu, E_p)/dz$ with respect to $\mu^{-2}E_t$. Note that a minus sign is necessary to make $d^2n(E_0, E_p)/dE_0 dz$ positive. Thus we have

$$d^2n(E_0, E_p)/dE_0 dz = -d^2n_1(\mu, E_p)/d\mu dz \times 1/(2\mu E_t). \quad (9)$$

After differentiation, all μ 's of r. h. s. should be replaced by a variable $E_0 (> E_t)$. Note that the secondaries are excited isotropically. Later, the calculated $d^2n(E_0, E_p)/dE_0 dz$ will be shown in fig.4 for several r_s values. Calculation brings us several features on $d^2n(E_0, E_p)/dE_0 dz$. The most remarkable one is that $d^2n(E_0, E_p)/dE_0 dz$ and $dn(E_0, E_p)/dz (= dn_1(\mu, E_p)/dz)$ are no more divergent at $E_0 = E_t$, due to the dynamical screening. This is a clear distinction from the results of Baroody³⁾ and Streitwolf⁴⁾.

2-3 Transport of excited secondaries

From fig.2, low-energy (< 30 eV) electrons have the relatively long mean free paths and are considered to lose only a small amount of their kinetic energy. Then, firstly, the continuous slowing down approximation on the assumption of a straight-line path is adopted here. Secondly, the elastic collision events between secondaries and target nucleus are ignored.

Let $P(E, E_0; z, \theta)$ represent the transport probability of excited secondaries moving on a straight-line trajectory from the created point with energy E_0 to the surface with energy E . In general, the propagation of particles in the material either accompanies or do not accompany the loss of kinetic energy. The propagator of the no-energy-loss case is found to have the form

$$P_{el}(E, E_0; z, \theta) = \exp(-z/\lambda(E)\cos\theta) \delta(E - E_0), \quad (10)$$

On the other hand, the propagator of the energy-loss case, $P_{inel}(E, E_0; z, \theta)$, is treated under the continuous slowing down approximation as

$$P_{inel}(E, E_0; z, \theta) = \delta(E - y(x)), \quad (11)$$

with

$$x = z/\cos\theta = -\int_{E_0}^y dE/S(E). \quad (12)$$

2-4 Transmission of the surface potential barrier

So far, the transmission of excited secondary electrons through the surface have been mainly treated classically, where the transmission probability $T(E, \theta; \phi)$ is always unity as long as secondaries have the kinetic energy E greater than the surface

barrier potential $U = E_f + \phi$. we have interest in the kinetic energy of SE's ranging from 0 to about 30 eV, where the reflection at the solid surface can not be neglected. Therefore the quantum-mechanical treatment was applied to the transmission problem. The surface potential barrier is assumed to be described by the step function. Then, we obtain¹⁴⁾

$$T_q(E, \theta; \phi) = 4(E \cos^2 \theta - \phi - E_f)^{1/2} (E \cos^2 \theta)^{1/2} \\ \times \{ (E \cos^2 \theta - \phi - E_f)^{1/2} + (E \cos^2 \theta)^{1/2} \}^{-2},$$

for $E \cos^2 \theta \geq \phi + E_f$. (13)

The critical angle θ_c in (13) is determined by

$$\theta_c = \cos^{-1} \{ (E_f + \phi) / E \}^{1/2}. \quad (14)$$

2-5 Angular and energy distributions of SE outside solids

Based on the above treatment, we arrive at the following results on the angular and energy distributions of SE's. The z dependence of the internal energy distribution of SE's is ignored since the kinetic energy of the primary electron does not change so much over the excited layers (several ten angstrom) which can contribute to the SE emission. Note that the solid angles inside and outside the surface denoted, respectively, by $d\Omega$ and $d\Omega'$, are connected with

$$\cos \theta d\Omega dE = E' / (E' + \phi + E_f) \cos \psi d\Omega' dE', \quad (15)$$

$$E = E' + E_f + \phi, \quad (16)$$

by considering the energy conservation relation. As a result, the total angular distribution of emitted secondaries is described by

$$d^2 \gamma' / dE' d\Omega' = \cos \psi d\Omega' / (4\pi) [\lambda(E') d^2 n(E', E_p) / dE' dz \\ + dn_1(E', E_p) / dz / S(E')] T_q(E', \psi; \phi) E' / (E' + E_f + \phi). \quad (17)$$

If one integrate $d^2 \gamma' / dE' d\Omega'$ over ψ , the total energy distribution outside the solid is reduced to be

$$d\gamma' / dE'$$

$$\begin{aligned}
&= [d^2 n(E', E_p) / dE' dz \lambda(E') + dn_1(E', E_p) / dz / S(E')] \\
&\times (1/3) \{ E' / (E' + E_F + \phi) \}^{3/2} [2 + \{ E' / (E' + E_F + \phi) \}^{1/2}] \\
&\times [\{ E' / (E' + E_F + \phi) \}^{1/2} + 1]^{-2}. \quad (18)
\end{aligned}$$

3. Numerical results and discussion.

First we have evaluated numerically the energy distributions of the internal SE's by the ion beam per unit primary path, i. e. , $d^2 n(E_0, E_p) / dE_0 dz$, and its integral over E_0 , $dn(E_0, E_p) / dz$. So far, the pure Coulomb interaction treatment^{3,4)} have been widely used²⁾. In this paper, we have included the dynamical screening effect into the estimation of this quantity. Figure 3 shows the shapes of $dn(E_0, E_p) / dz$ versus the kinetic energy of SE for various proton energy E_p penetrating an electron gas with $r_s = 2.0$, where the curves are normalized at the maximum value. Figure 4 shows the corresponding $d^2 n(E_0, E_p) / dE_0 dz$ curves, which is obtained according eq. (9). Regarding the normalized $d^2 n(E_0, E_p) / dE_0 dz$ curves, one can see a remarkable feature. That is, the shape of $d^2 n(E_0, E_p) / dE_0 dz$ as a function of excited energy E_0 are almost the same up to $E_0 = 100$ eV. In order to see the absolute values, $d^2 n(E_0, E_p) / dE_0 dz$ and $dn(E_0, E_p) / dz$ at the energy $E_0 = E_t$ (the peak position) for $r_s = 2.0$ are plotted in fig. 5.

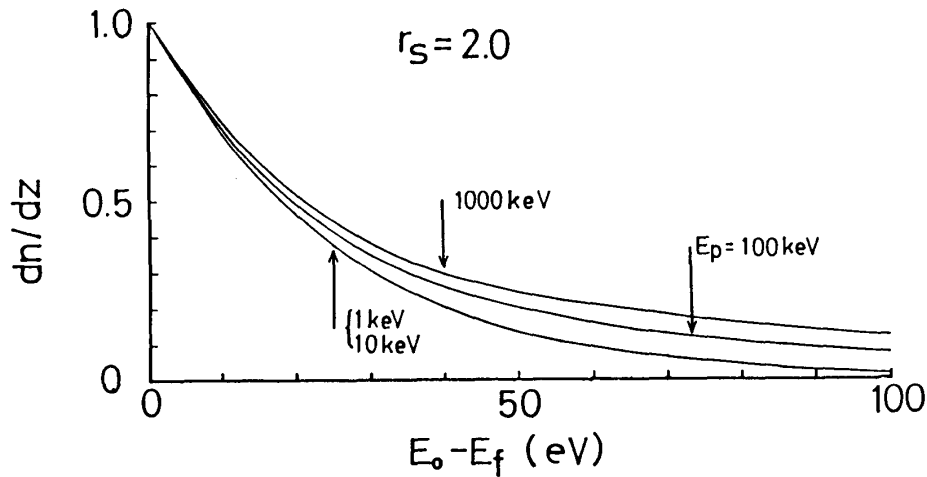


Fig. 3 The normalized $dn(E_0, E_p) / dz$ inside a solid with $r_s = 2$ under the bombardment of protons with E_p .

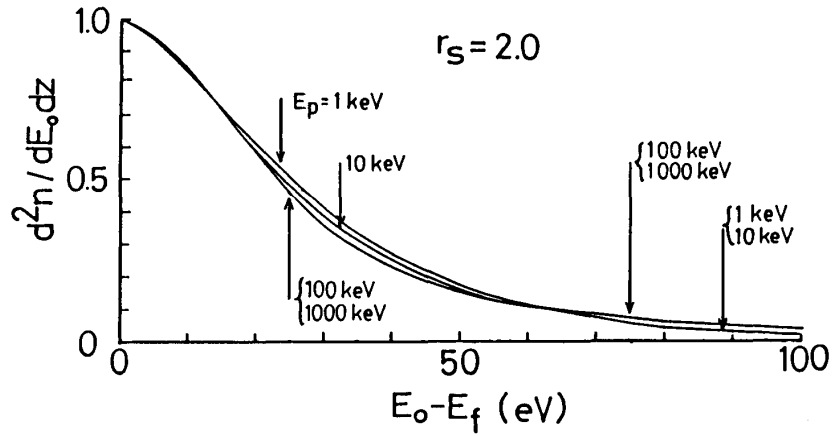


Fig. 4 The normalized $d^2n(E_0, E_p)/dE_0 dz$ inside a solid with $r_s = 2$ under the bombardment of protons with E_p .

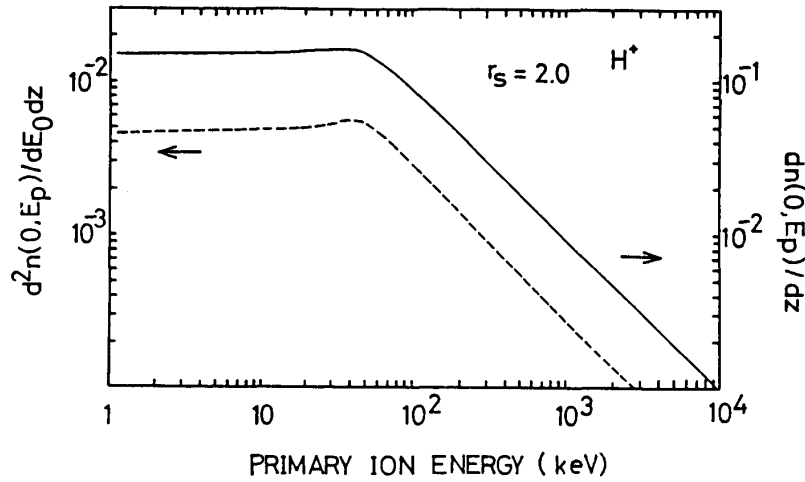


Fig. 5 The values of $d^2n(E_0, E_p)/dE_0 dz$ and $dn(E_0, E_p)/dz$ at $E_0 = E_f$ against the proton energy E_p for $r_s = 2$.

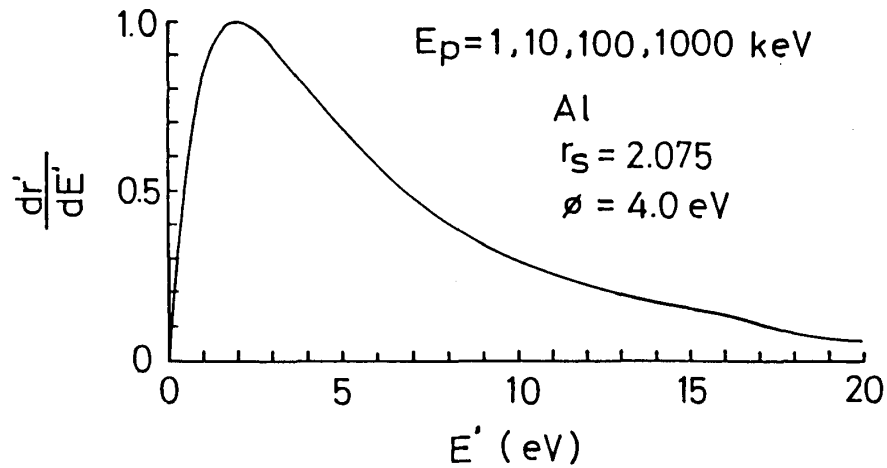


Fig. 6 The normalized SE energy distribution, $d\gamma'/dE'$, emitted from an Al target with $r_s = 2.075$ and $\phi = 4.0$ eV bombarded by a proton of normal incidence.

In our treatment the r_s value and the work function ϕ of the material are necessary to calculate the energy distribution, $d\gamma'/dE'$, of the emitted secondary electrons. Figure 6 shows the calculated $d\gamma'/dE'$ curve for a proton incident on an Al metal having $r_s = 2.075$ and $\phi = 4.0$ eV. The peak of the calculated $d\gamma'/dE'$ is located at $E' = 2.0$ eV and the width of the half maximum is 6.3 eV, which is almost the same as under the high energy (3 keV) electron bombardment^{15),16)}. It should be noted that this profile does not change appreciably with E_p values investigated. Judging from the weak dependence of the normalized $d^2n(E_0, E_p)/dE_0dz$ upon E_p , we can conclude that both the peak position and the width of $d\gamma'/dE'$ calculated for an Al are almost independent of E_p in the region of $E_p > 500$ eV.

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References

- 1) A. J. Dekker, in "Solid State Physics" (Prentice-Hall Inc. , N. J. , 1957) Chap. 17.
- 2) G.F.Amelio, J. Vac. Sci. and Tech. 7, 593 (1970) .
- 3) E. M. Baroody, Phys. Rev. 78, 780 (1950) .
- 4) H. W. Streitwolf, Ann. Phys. (Leipz.) 3, 183 (1959) .
- 5) L. V. Spencer, Phys. Rev. 98, 1597 (1955) .
- 6) T. E. Everhard, N. Saeki, R. Shimizu, and T. Koshikawa, J. Appl. Phys. 47, 2941 (1976) .
- 7) R. Bindi, H. Lanteri, and P. Rostaing, J. Phys. D13, 267 (1980) .
- 8) J. Schou, Phys. Rev. B22, 2141 (1980) .
- 9) G. Bachmann, J. Scholtes, and H. Oechsner, Mikrochim. Acta [Wien] I, 489 (1987) ; Fresenius. Z. Anal. Chem. 329, 195 (1987) .
- 10) M. S. Chung and T. E. Everhart, J. Appl. Phys. 45, 707 (1974) .
- 11) J. C. Ashley, C. J. Tung, and R. H. Ritchie, Surf. Sci. 81, 409 (1979) .
- 12) J. Quinn and R. Ferrell, Phys. Rev. 112, 812 (1958) .
- 13) J. Lindhard and A. Winther, K. Dan. Vidensk. Selsk. Mat. Fys. Medd. 34, 1 (1964) no. 4 .
- 14) L. Landau and E. Lifshitz, "Quantum Mechanics" (Addison-Wesley, Mass. , 1958) .
- 15) T. Kaneko, G. Bachmann, W. Berthold and H. Oechsner, to be published.
- 16) T. Kaneko, to be published.