Determination of differential surface excitation parameters from experimental reflection-electron-energy-loss spectra

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Within the framework of dielectric response theory, it is found that the inelastic interaction can be characterized by the differential inverse inelastic mean free path (DIIMFP) for bulk excitations and the differential surface excitation parameter (DSEP) for surface effects. Based on transport theory, the inelastic scattering cross section $K(E_o \rightarrow E_o - \omega)$ experimentally determined from reflection-electron-energy-loss spectroscopy (REELS) can be related to the bulk DIIMFP and DSEP. From this relation, a method to derive the bulk DIIMFP and DSEP from experimental $K(E_o \rightarrow E_o - \omega)$ is proposed.

1. INTRODUCTION

Electron energy loss spectroscopy in the reflection mode (REELS) has been widely used as a surface and interface analysis tool [1-6] which provides information on the electronic and optical properties of the solid. Also, REELS spectra carry valuable information about the inelastic scattering properties of medium energy electrons (200 eV - 2000 eV) near the solid surface. This information is both of fundamental and practical importance due to the fact that the quantitative electron spectroscopies, like Auger eletron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS), must rely heavily on detailed knowledge of the inelastic scattering properties.

Tougaard and coworkers [7-10] have pioneered the application of reflection electron energy loss spectroscopy (REELS) experiments to gain knowledge about inelastic scattering cross sections, $K(E_o \rightarrow E_o - \omega)$. Here E_o is the incident electron energy and ω is the electron-energy loss. The experimentally determined $K(E_o \rightarrow E_o - \omega)$ are significantly different from the conventional differential inverse inelastic mean free path (DIIMFP) for bulk excitations due to the surface effects [10-13]. The method of Tougaard and Chorkendorff becomes especially attractive because the determined DIIMFP may be applied to remove the inelastic background signal from AES or XPS spectra [7,8,12,13]. However, an inherent problem is that $K(E_o \rightarrow E_o - \omega)$ determined from REELS data contain information associated with electrons traversing the solid-vacuum surface twice while, in the AES or XPS measurement, the signal electrons traverse this surface only once. As a result, the intensities associated with the surface excitations in REELS spectra are enhanced with respect to the AES or XPS measurement [14,15].

In this work, the DIIMFP is theoretically divided into a bulk and a surface term. The bulk term is the DIIMFP in an infinite medium, while the surface term is spatially varying on both sides of the vacuum-solid surface. Since surface effects are restricted to a surface layer on the order of several angstroms, these effects can be described by the differential surface excitation parameter (DSEP) which is the integration of the surface term in the DIIMFP. Based on transport theory, the experimental $K(E_o \rightarrow E_o - \omega)$ can be related to the bulk DIIMFP and DSEP. With this derived relation, the bulk DIIMFP and DSEP can be directly determined using the experimental $K(E_o \rightarrow E_o - \omega)$ at two different primary electron energies without any other input parameter.

2. INELASTIC INTERACTIONS IN SOLID SURFACES

We have recently derived the spatially varying DIIMFP of an electron penetrating into vacuum from a solid for quantitative analysis of XPS [16,17]. Here we presented the general formula that include the incoming (IN) and outgoing (OUT) trajectories. The notation $v = |v|$, $q = (Q, q_z)$, $v = (v_{||}, v_z)$, and $r = (R, z)$, where

Q, $v_{||}$, and R represent components parallel with the interface, will be adopted hereafter.

The vacuum-solid system is the typical case in REELS experiment. Here the solid is considered to be contained in the region $z<0$. With the dielectric theory, the DIIMFP can be split into a bulk and a surface term. For an electron of energy $E=v^2/2$ to lose energy ω, the spatially varying differential inverse inelastic mean free path (DIIMFP), $\mu(E\to E-\omega,\alpha,z)$, for the IN and OUT trajectories in the vacuum-solid system can be respectively expressed as

$$\mu^{IN}(E\to E-\omega,\alpha',z) = \mu_B(E\to E-\omega)+\mu_S^{IN}(E\to E-\omega,\alpha',z) \quad (1)$$

and

$$\mu^{OUT}(E\to E-\omega,\alpha,z) = \mu_B(E\to E-\omega)+\mu_S^{OUT}(E\to E-\omega,\alpha,z), \quad (2)$$

where

$$\mu_B(E\to E-\omega)=\frac{1}{\pi^2 v}\left\{\int d^2Q\frac{|v_z|}{\tilde{\omega}^2+(v_zQ)^2}\times\mathrm{Im}\left[-\frac{\Theta(-z)}{\varepsilon(\tilde{q},\omega)}\right]\right\}, \quad (3)$$

$$\mu_S^{IN}(E\to E-\omega,\alpha',z)=\frac{1}{\pi^2 v}\int d^2Q\times\frac{|v_z|}{\tilde{\omega}^2+(v_zQ)^2}\mathrm{Im}\left[\Pi_S^{IN}(v,z,Q,\omega)\right] \quad (4)$$

and

$$\mu_S^{OUT}(E\to E-\omega,\alpha,z)=\frac{1}{\pi^2 v}\int d^2Q\times\frac{|v_z|}{\tilde{\omega}^2+(v_zQ)^2}\mathrm{Im}\left[\Pi_S^{OUT}(v,z,Q,\omega)\right], \quad (5)$$

where

$$\Pi_S^{IN}(v,z,Q,\omega) = e^{-Q|z|}\left[\frac{\bar{\varepsilon}(Q,\omega)}{\varepsilon(\tilde{q},\omega)}\frac{\varepsilon(\tilde{q},\omega)-1}{\bar{\varepsilon}(Q,\omega)+1}\right]\times\left[e^{-Q|z|}\Theta(z)-\frac{\left(2\cos(\tilde{\omega}z/v_z)-e^{-Q|z|}\right)\Theta(-z)}{\bar{\varepsilon}(z,Q,\omega)}\right], \quad (6)$$

and

$$\Pi_S^{OUT}(v,z,Q,\omega) = e^{-Q|z|}\left[\frac{\bar{\varepsilon}(Q,\omega)}{\varepsilon(\tilde{q},\omega)}\frac{\varepsilon(\tilde{q},\omega)-1}{\bar{\varepsilon}(Q,\omega)+1}\right]\times\left[\left(2\cos(\tilde{\omega}z/v_z)-e^{-Q|z|}\right)\Theta(z)-\frac{e^{-Q|z|}\Theta(-z)}{\bar{\varepsilon}(z,Q,\omega)}\right]. \quad (7)$$

Here $\tilde{\omega}=\omega-v_{||}\cdot Q$; $\tilde{q}^2=Q^2+\tilde{\omega}^2/v_z^2$; $\Theta(z)$ is the Heaviside step function; α is the angle between the electron velocity and positive z-axis; $\alpha'=\pi-\alpha$ is the angle between the electron velocity and negative z axis. The bulk term $\mu_B(E\to E-\omega)$ which is independent of the position and emission angle gives rise to the well known expression of the DIIMFP of electrons moving in an infinite medium [18]. On the other hand, the surface term is not confined to the interior of the solid, but also takes place, while the electron is at some distance outside the surface.

The energy and momentum conservation can be included by limiting the range of integration over Q as follows:

$$q_-^2\le(\tilde{\omega}/v_z)^2+Q^2\le q_+^2 \quad , \quad (8)$$

where $q_\pm=\sqrt{2E}\pm\sqrt{2(E-\omega)}$. The model dielectric function developed in previous work is used to investigate the inelastic electron interaction near a solid surface., i.e., [16, 17]

$$\varepsilon(q,\omega)=\varepsilon_b-\sum_j\frac{A_j}{\omega^2-\left(\omega_j+q^2/2\right)^2+i\omega\gamma_j} \quad (9)$$

where ε_b is the background dielectric constant due to the effect of polarizable ion cores and A_j, γ_j and ω_j are, respectively, the oscillator strength, damping coefficient, and excitation energy, all associated with the jth oscillator.

Although the DIIMFP depends on electron direction and distance from the surface, the angular dependence is indeed rather weak. Therefore, the

results presented here are for the case of an electron moving in the direction perpendicular to the surface. Figures 1 (a) and (b), respectively, show the position dependence of the calculated DIIMFPs for a normally escape electron with E=1 keV inside and outside Cu. The results show that the surface effects have a rather limited extent at a distance on the order of several Ångström.

Since the surface effects have a rather limited extent about the surface, they can be practically characterized by the differential surface excitation parameter (DSEP) that is calculated via integration of DIIMFP,i.e.

$$P_S^{IN,OUT}(E \to E-\omega,\alpha) = \int_{-\infty}^{\infty} \frac{dz}{\cos\alpha} \mu_S^{IN,OUT}(E \to E-\omega,\alpha,z), \qquad (10)$$

Even though the interval of the integration in Eq. (10) is infinite, the effective contribution is restricted to a limited region extending on both sides of the vacuum-solid surface. In other words, the DSEP includes the total surface effects for an electron penetrating through the effective region of surface excitations, which is around several Ångström.

With the model dielectric function, we have calculated the bulk DIIMFP and DSEP. Figure 2 shows $\mu_B(E \to E-\omega)$ evaluated from Eq. (3) for electrons with various energies in Au. Although the bulk DIIMFP in general decreases with increasing the electron energy, the structures and peak positions of the bulk DIIMFP are not sensitive to variation in E. Therefore, one might expect the energy loss dependence of the product $\lambda_B(E)\mu_B(E \to E-\omega)$ is nearly the same for different electron energies due to the fact that the equality $\int_0^E d\omega\, \lambda_B(E)\mu_B(E \to E-\omega) = 1$ holds according to the definition: $\lambda_B(E) = \left[\int_0^E d\omega\, \mu_B(E \to E-\omega)\right]^{-1}$.

Based on this property, the product $\lambda_B(E)\mu_B(E \to E-\omega)$ can be practically expressed as

$$\lambda_B(E)\mu_B(E \to E-\omega) = \mu_B^{\circ}(\omega) \qquad (11)$$

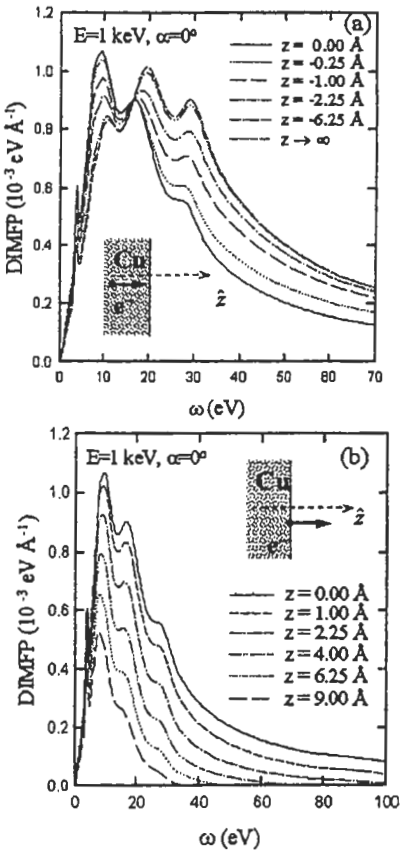

Figure 1. The position dependence of the calculated DIIMFPs for a normally escape electron with E=1 keV (a) inside and (b) outside Cu.

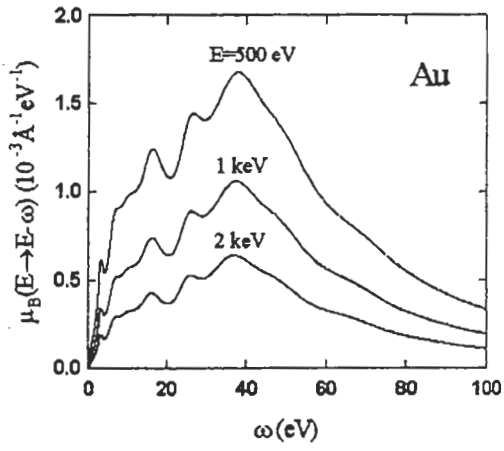

Figure 2 The calculated bulk DIIMFP for electrons with various energies in Au.

where $\mu_B^{\circ}(\omega)$ is independent of E and represents a normalized probability density function for bulk excitation. The probability density function $\mu_B^{\circ}(\omega)$ is one of the fundamental ingredients in Monte Carlo simulations. For convenience, we call $\mu_B^{\circ}(\omega)$ the "reduced DIIMFP" hereafter.

Fig. 3 depicts the energy loss dependence of the DSEP for normal incident electrons with various energies in Cu. This DSEP includes the total surface effects for a electron penetrating through the effective region of surface excitations which is about 3~6 Å for a 1-keV electron. It is seen that surface excitations contribute largely at small energy losses as compared to bulk excitations. Similar to the property of $\mu_B(E \to E-\omega)$, the structures and peak positions of $P_S(E \to E-\omega,\alpha)$ are also insensitive to variation in E. The calculated results show that the DSEP approximately proportional to $1/\sqrt{E}$. This tendency coincides with the prediction of the free-electron-gas model. In other words, the distribution of $\sqrt{E}P_S(E \to E-\omega,\alpha)$ is almost independent of E. This characteristic enables us to separate E-dependence from $P_S(E \to E-\omega,\alpha)$ and to write

$$P_S(E \to E-\omega,\alpha) = \frac{1}{\sqrt{E}} P_S^{\circ}(\omega,\alpha) \qquad (12)$$

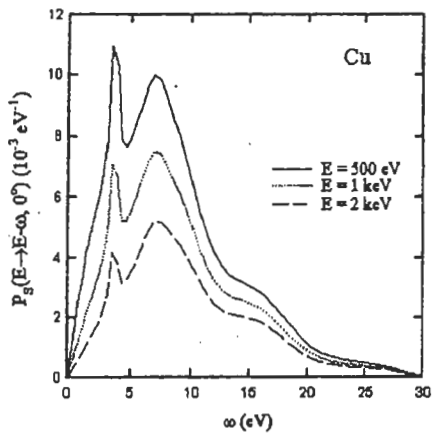

Figure 3 The energy loss dependence of the DSEP for normal incident electrons with various energies in Cu.

Hereafter we call $P_S^{\circ}(\omega,\alpha)$ the "reduced DSEP".

Detailed knowledge of the bulk DIIMFP and DSEP is important for quantitative analysis by surface electron spectroscopies. Eqs. (3) and (10) can be employed to calculate inelastic scattering cross sections when the dielectric-response function of the particular solid is known in detail with respect to the energy transfer. However, literature data for dielectric-response functions are usually not available. Therefore it is of high interest to be able to obtain the DIIMFP and DSEP experimentally. It can be seen later that Eqs. (11) and (12) play a practical role in determining such cross sections from REELS data.

3. Derivation of DIIMFP and DSEP from REELS spectra

The algorithm developed by Tougaard and Chorkendorff [7] in determining experimental differential inelastic-electron-scattering cross sections $K(E_o \to E_o-\omega)$ from REELS spectra is based on the following formula

$$j(E_o;E) = \int_{-\infty}^{\infty} \frac{ds}{2\pi} \frac{\exp[i(E_o-E)s]}{1-\dfrac{L\lambda(E_o)}{L+\lambda(E_o)}\tilde{K}(E_o;s)} \qquad (13)$$

where $\tilde{K}(E_o;s)$ is the Fourier transform of $K(E_o \to E_o-\omega)$ with respect to ω, and $\lambda(E_o)$ is defined as

$$\lambda(E_o) = \int_0^{E_o} K(E_o \to E_o-\omega)d\omega . \qquad (14)$$

From transport theory, the relationship between the experimental $K(E_o \to E_o-\omega)$ and the bulk DIIMFP and DSEP is given by

$$1-\frac{L\lambda(E_o)}{L+\lambda(E_o)}K(E_o;s) = \left[1-\frac{L\lambda_B(E_o)}{L+\lambda_B(E_o)}\tilde{\mu}_B(E_o;s)\right] \times \exp\left[-\tilde{P}_S(E_o,\alpha_I,\alpha_R;s)\right] \qquad (15)$$

where $\omega = E_o - E$, $\tilde{\mu}_B(E_o;s)$ is the Fourier transform of $\mu_B(E_o \to E_o-\omega)$ with respect to ω, and $\tilde{P}_S(E_o,\alpha;s)$ is the Fourier transform of $P_S(E_o \to E_o-\omega,\alpha)$ with respect to ω. The angular dependence of $P_S(E_o \to E_o-\omega,\alpha)$ results in the fact that the experimentally obtained $K(E_o \to E_o-\omega)$ depends on both the angle of incidence and exist angle of the electrons. Taking $P_S(E_o \to E_o-\omega,\alpha) = 0$,i.e. neglecting the surface effects, we can get $\lambda = \lambda_B$ and $K(E_o \to E_o-\omega) = \mu_B(E_o \to E_o-\omega)$. This is reason why $K(E_o \to E_o-\omega)$ determined from REELS spectra is often treated as a single scattering cross section.

In general $L >> \lambda$, therefore Eq. (15) can be simplified as

$$1-\lambda(E_o)K(E_o;s)=[1-\lambda_B(E_o)\tilde{\mu}_B(E_o;s)] \times\exp[-\tilde{P}_S(E_o,\alpha_I,\alpha_R;s)] \quad (16)$$

Eq. (16) indicates that the cross section $\lambda(E_o)K(E_o \rightarrow E_o-\omega)$ obtained from REELS data cannot expressed as a linear combination of pure bulk and pure surface components. Introducing Eqs. (11) and (12) into Eq. (16), we can obtain

$$1-\lambda(E_o)K(E_o;s)=[1-\mu_B^o(s)] \times\exp[-\tilde{P}_S^o(\alpha_I,\alpha_R;s)/\sqrt{E_o}], \quad (17)$$

with

$$\tilde{P}_S^o(\alpha_I,\alpha_R;s)=\tilde{P}_S^o(\alpha_I;s)+\tilde{P}_S^o(\alpha_R;s) \quad (18)$$

where $\mu_B^o(s)$ and $\tilde{P}_S^o(\alpha;s)$ are, respectively, the Fourier transform of $\mu_B^o(\omega)$ and $P_S^o(\omega,\alpha)$ with respect to ω.

To directly determine the bulk DIIMFP and DSEP from REELS data, we use the experimental $\lambda(E_o)K(E_o;s)$ obtained at two different primary electron energies, $E_o=E_1$ and $E_o=E_2$. From Eq. (17) we can write the pair equation

$$1-\lambda(E_1)K(E_1;s)=[1-\mu_B^o(s)] \times\exp[-\tilde{P}_S^o(\alpha_I,\alpha_R;s)/\sqrt{E_1}] \quad (19)$$

and

$$1-\lambda(E_2)K(E_2;s)=[1-\mu_B^o(s)] \times\exp[-\tilde{P}_S^o(\alpha_I,\alpha_R;s)/\sqrt{E_2}]. \quad (20)$$

Taking the logarithm of both sides of Eq. (19) and (20), after some algebra, we can obtain

$$\tilde{P}_S^o(\alpha_I,\alpha_R;s)=\frac{\sqrt{E_1E_2}}{\sqrt{E_2}-\sqrt{E_1}}\ln\left[\frac{1-\lambda(E_2)K(E_2;s)}{1-\lambda(E_1)K(E_1;s)}\right], \quad (21)$$

and

$$\mu_B^o(s)=1-\exp\left\{\frac{\sqrt{E_2}\ln[1-\lambda(E_2)K(E_2;s)]-\sqrt{E_1}\ln[1-\lambda(E_1)K(E_1;s)]}{\sqrt{E_2}-\sqrt{E_1}}\right\} \quad (22)$$

Therefore, Eqs. (21) and (22) can be used to determine the bulk DIIMFP and DSEP by means of the fast Fourier transform (FFT) algorithm, provide that $\lambda(E_1)K(E_1;s)$ and $\lambda(E_2)K(E_2;s)$ are given.

To avoid significant errors introduced by the approximations, the appropriate ranges for E_1 and E_2 are around 0.4~1.5 keV and 2~10 keV, respectively. If both E_1 and E_2 are higher than 3-keV, the surface effects may be too small to be used in Eqs. (21) and (22). On the other hand, the first Born approximation presented here needs to be modified as the electron energy lower than 0.3-keV.

4. Conclusions

The inelastic scattering cross section of electrons with solid surfaces has been derived with the approach of dielectric response theory. It is shown that the inelastic scattering cross section includes the bulk DIIMFP and DSEP. The relation between the experimental $K(E_o \rightarrow E_o-\omega)$ from REELS data and the bulk DIIMFP and DSEP has been obtained through including surface effects into the Landau formula. Based on this relation, a method to derive the bulk DIIMFP and DSEP from REELS data has been proposed. The only input is the experimental $K(E_o \rightarrow E_o-\omega)$ at two different primary electron energies.

5. References

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