Applied Surface Science 356 (2015) 142–149

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Surface excitation parameter for rough surfaces

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ARTICLE INFO

Article history:
Received 24 June 2015
Received in revised form 4 August 2015
Accepted 6 August 2015
Available online 8 August 2015

Keywords:
Surface roughness
Surface excitation parameter
EPES
Monte Carlo simulation

ABSTRACT

In order to assess quantitatively the importance of surface excitation effect in surface electron spectroscopy measurement, surface excitation parameter (SEP) has been introduced to describe the surface excitation probability as an average number of surface excitations that electrons can undergo when they move through solid surface either in incoming or outgoing directions. Meanwhile, surface roughness is an inevitable issue in experiments particularly when the sample surface is cleaned with ion beam bombardment. Surface roughness alters not only the electron elastic peak intensity but also the surface excitation intensity. However, almost all of the popular theoretical models for determining SEP are based on ideal plane surface approximation. In order to figure out whether this approximation is efficient or not for SEP calculation and the scope of this assumption, we proposed a new way to determine the SEP for a rough surface by a Monte Carlo simulation of electron scattering process near to a realistic rough surface, which is modeled by a finite element analysis method according to AFM image. The elastic peak intensity is calculated for different electron incident and emission angles. Assuming surface excitations obey the Poisson distribution the SEPs corrected for surface roughness are then obtained by analyzing the elastic peak intensity for several materials and for different incident and emission angles. It is found that the surface roughness only plays an important role to SEP only for large interaction angle cases (larger than 60°) and large surface roughness (root-mean-square value lager than 15 nm). This result is a clear evidence that the SEP database calculated based on ideal plane surface model are still efficient for realistic sample surface with common surface roughness.

1. Introduction

A precise knowledge of electron inelastic mean free path (IMFP) is essential to surface quantification by surface electron spectroscopies, such as, X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), elastic peak electron spectroscopy (EPES) and reflection electron energy loss spectroscopy (REELS). IMFP can be derived from EPES measurement [1–3] in conjunction with a Monte Carlo (MC) simulation. However, a deviation on IMFP values between theoretical calculation and experimental measurement has been found; it is attributed to several possible factors, e.g. accuracy of electron elastic scattering cross-sections [4] for a MC simulation, choice of the dielectric function model for [5] for a MC simulation and IMFP calculation, neglect of surface excitation effect and influence of surface roughness [1,6]. Early studies [7–10] have shown that a preponderant reason for this deviation is due to surface excitations, while some recent researches [11,12] have revealed that, although it weakly affects the deviation directly, surface roughness can modify the surface excitation and to exert an influence indirectly. However, almost all of the past theoretical studies for calculating surface excitation parameter (SEP), are based on the ideal plane surface approximation, including the most popular user-friendly software, Quantitative Analysis of Electron Energy Losses at Surface (QUEELS) [13]. Therefore, to investigate the scope of application of these two software as well as other theoretical models based on ideal plane surface approximation, it is necessary to have a quantitative knowledge of the surface roughness effect on surface excitation. The purpose of this work is to calculate SEP corrected by surface roughness by means of evaluating elastic peak intensity, thus evaluating the SEP data calculated by ideal plane surface model as well as the efficient suitable range for these data.

SEP is a factor for evaluation of surface excitation probability. There are two different definitions of SEP. It is usually defined as an average number of surface excitations that an electron undergoes

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http://dx.doi.org/10.1016/j.apsusc.2015.08.056
0169-4332/

when it crosses the surface once [14–16]. However, this definition has not taken into account of the Begrenzungs effect, i.e., the decrease in the bulk excitation probability accompanying increase in surface excitation probability when electrons are close to the surface for the bulk- and surface-modes are orthogonal [17]. Therefore, SEP calculated by this definition cannot be used directly as a correction factor to the elastic peak intensity, with which IMFP can be obtained with the EPES method. On the other hand, in both theoretical [18] and experimental [3] studies SEP has been defined as the change in the excitation probability caused by the presence of the surface in comparison with the situation where an electron travels in an infinite medium. The SEP by this definition can be practically used to the EPES analysis for determination of IMFP. Therefore, in this work, SEP is calculated by the latter definition from the elastic peak intensity obtained by MC simulation only considering bulk excitation or including surface excitation. Furthermore, we have introduced a rough surface model into MC simulation and the elastic peak intensities are obtained on different rough surfaces instead of a planar surface, which enables SEPs corrected for surface roughness are obtained.

The problem of surface roughness influence to surface analysis has been investigated theoretically and experimentally [19–23]. However, little simulation work has been done as it is difficult to deal with the surface roughness theoretically in a general form, even in the case without considering surface excitation. This is because the fact that practical samples may present various kinds of surface topographies which may complicate mathematical modeling for a MC simulation. In our previous works [11,12,24], we have used a finite element method to build a full 3D rough surface model, whose character was extracted from AFM images of real sample surfaces, and the influence of surface topography to elastic peak intensity has been studied by neglecting surface excitation effect [24]; a surface roughness parameter (SRP) was introduced to quantify the roughness effect. Then, we have also investigated surface excitation together with surface roughness by REELS and EPES spectra of rough surfaces, and it has been found that surface roughness modifies surface excitation strongly, especially in low energy region [11,12]. Therefore, to obtain surface roughness dependent SEP, MC simulations of angle-resolved EPES have been performed in this work by incorporating such a surface topography modeling and also including surface excitation on the modeled rough surfaces. The simulated results are found to agree well with the experimental data.

2. Theoretical methods

2.1. Electron elastic scattering

In this study, the Mott's cross section [25],

$$\frac{d\sigma}{d\Omega} = |f(\vartheta)|^2 + |g(\vartheta)|^2, \tag{1}$$

is employed for the treatment of electron elastic scattering, where the scattering amplitudes,

$$\begin{aligned} f(\vartheta) &= \frac{1}{2iK}\sum_{\ell=0}^{\infty}\{(\ell+1)(e^{2i\delta_\ell^+}-1)+l(e^{2i\delta_\ell^-}-1)\}P_\ell(\cos\vartheta); \\ g(\vartheta) &= \frac{1}{2iK}\sum_{\ell=1}^{\infty}\{-e^{2i\delta_\ell^+}+e^{2i\delta_\ell^-}\}P_\ell^1(\cos\vartheta), \end{aligned} \tag{2}$$

are calculated by the partial wave expansion method [26]. In the above equation $P_\ell(\cos\vartheta)$ and $P_\ell^1(\cos\vartheta)$ are, respectively, the Legendre and the first-order associated Legendre functions. δ_ℓ^+ and δ_ℓ^- are spin-up and spin-down phase shifts of the ℓth partial wave, respectively. The phase shifts are numerically evaluated by solving the Dirac equation for the radial part of the wave function of the scattered electron. The Thomas-Fermi-Dirac atomic potential [27] is used in the calculation.

2.2. Inelastic scattering

First, we consider an electron at a position $\mathbf{r} = \mathbf{v}t$ relative to the crossing point at the surface, moving with a velocity $\mathbf{v} = (\mathbf{v}_\parallel, v_\perp),$, where $v_\perp$ is positive for an electron approaching the surface from the bulk. The solid medium, characterized by its dielectric function $\varepsilon(\mathbf{q}, \omega)$ from the dielectric response theory, is considered to occupy a semi-infinite space of $z<0$ with the surface boundary defined at $z=0$. In the specular surface reflection model [27,28] the induced potential is determined by the real charge, its image charge, and the fictitious surface charges fixed by the boundary conditions. The image charge and the surface charges are responsible for the surface effect of electron inelastic scattering in the surface region.

General discussions on the surface response function and the electron self-energy have been made previously [29–32]. Assuming a vanishing surface potential and a fast-electron approximation, the random-phase-approximation self-energy of an inhomogeneous system is expressed in terms of the bulk dielectric function of the specimen, the corresponding differential self-energy inhomogeneous in the z-direction for various positions and directions of moving electrons is provided as follows:

$$\sum(z|\omega) = \begin{cases} \Sigma_1(z|\omega) & z>0, v_\perp<0 \\ \Sigma_{bulk}(\omega)+\Sigma_i(z|\omega)+\Sigma_s(z|\omega)+\Sigma_{i-s}(z|\omega) & z<0, v_\perp<0 \\ \Sigma_1(z|\omega)+\Sigma_2(z|\omega) & z>0, v_\perp>0 \\ \Sigma_{bulk}(\omega)+\Sigma_i(z|\omega)+\Sigma_s(z|\omega) & z<0, v_\perp>0 \end{cases}, \tag{3}$$

where Σ_{bulk}, $\Sigma_i(z|\omega)$, $\Sigma_s(z|\omega)$ and $\Sigma_{i-s}(z|\omega)$ are respectively the position independent bulk term, the image charge term, the surface charge term and the interference term between the image charge and the surface charges [33,34]. Therefore, in the case of an electron inside the solid and moving toward the surface ($z<0, v_\perp>0$), the image charge term and the surface charge term are found to represent the net surface effect. In the case of an incident situation ($z<0, v_\perp<0$), the surface terms are complicated in form by the interference of the image charge and the surface charges which leads to an extra term, $\Sigma_{i-s}(z|\omega)$. When an electron is in the vacuum region, $\Sigma_1(z|\omega)$ is the classical self-energy for an electron incident onto and escaping from the surface, and the extra term now is $\Sigma_2(z|\omega)$, which also contains the contribution from both the image charge and the surface charges. Then a differential inverse inelastic mean free path (DIIMFP) may be obtained numerically by the imaginary part of the differential self-energy:

$$\sigma_{total}(\omega|E,\alpha,z) = -\frac{2}{v}Im\left\{\sum(\omega|\alpha,z)\right\}. \tag{4}$$

It is reasonable that the total DIIMFP are inhomogeneous in the z-direction. Inverse IMFP can be easily calculated numerically by an integration of DIIMFP over energy loss ω. The above model is referred to as the "surface model" hereinafter. When only the bulk term Σ_b is considered, the model is reduced to the conventional model of bulk excitation and referred to as the "bulk model".

2.3. Surface roughness

In this work we use the root-mean-square (RMS) to quantify random surface roughness, which is measured by taking an average of