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Surface energy loss processes in XPS studied by absolute reflection electron energy loss spectroscopy

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ABSTRACT

The results of the investigation of the inelastic interaction of 300–3000 eV electrons with the Ni and Au surfaces by the analysis of absolute reflection electron energy loss spectroscopy (REELS) spectra were described. The present analysis enables the inelastic mean free path (IMFP), surface excitation parameter (SEP) and differential SEP (DSEP) to be obtained simultaneously from an absolute REELS spectrum. The obtained IMFPs for Ni and Au showed a good agreement with those calculated using the TPP-2M predictive equation. The present SEPs determined for Ni and Au were fitted to the Chen's formula describing the dependence of the SEP on the electron energy, and material parameters for Ni and Au in Chen's formula were proposed. The present DESPs were compared with the theoretical results, and a reasonable agreement between the experimentally determined DSEPs and theoretical results was confirmed. The MC modeling of calculating the REELS spectrum, in which energy loss processes due to surface excitations are taken into account, was also described. The IMFP, SEP and DSEP determined by the present absolute REELS analysis were employed to describe energy loss processes by inelastic scattering in the proposed MC simulation. The simulated REELS spectra were found to be in a good agreement with the experimental spectra for both Ni and Au.

1. Introduction

Quantitative information on the inelastic interaction of sub-keV to a few keV photoelectrons with the solid surface is of importance for quantitative surface chemical analysis using X-ray photoelectron spectroscopy (XPS). It is well known that the inelastic mean free path (IMFP) is one of the most important factors for quantitative XPS analysis since it describes the decay of the intensity of photoelectron peaks induced by inelastic interactions of signal photoelectrons with the solid surface. In addition, surface excitations have been recently proven to play an important role in energy loss processes due to inelastic interaction of photoelectrons with the solid surface. The surface excitation also introduces the significant decay of the intensity of signal electrons [1], and should be taken into consideration in quantification. The decay of the peak intensity due to surface excitations is described by the surface excitation parameter (SEP) [1,2].

For quantification by XPS, not only the decay of the photoelectron peak intensity itself but also the subtraction of the background appearing in the higher binding energy side of the photoelectron peak are important issues to be concerned. The background consists of electrons loosing their kinetic energy through bulk and surface excitations. Since the shape of the background is determined by the shape of the normalized differential IMFP (DIMFP) and differential SEP (DSEP) describing the energy loss probabilities due to bulk and surface excitations, respectively, and their contributions to the background, knowledge on the DIMFP and DSEP is also important for quantification.

Such interactions of signal electrons with solids have been intensively studied, and the determination of parameters such as the IMFP, SEP, DSEP, has been performed from both the experimental and theoretical points of view. Among experimental approaches, one of the most widely used approaches for such studies is the elastic peak electron spectroscopy (EPES) analysis [1,3–5]. Another experimental approach is the reflection electron energy loss spectroscopy (REELS) spectrum analysis [6–12].

The EPES analysis [13,14] has been widely applied to the experimental evaluation of the IMFP calculated by the TPP-2M predictive equation [15–21], which is one of the most widely used values of IMFPs. In most EPES studies dealing with the experimental determination of the IMFP, a reference material is required, the IMFP of which should be known, indicating that the IMFP obtained by

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the EPES analysis strongly depends on the selection of the reference material and the value of the IMFP used as the reference in the analysis [22–24]. In addition, since the decay of the elastic peak by surface excitations in the EPES analysis is significant [1], several EPES studies have been carried out by correcting the decay of the elastic peak intensity by surface excitations using predictive equations for the SEP [3,4]. These results revealed that the obtained IMFPs depend on the predictive equation for the SEP as well as the reference material and its IMFP.

The EPES analysis can also be applied to the determination of the SEP using the reference material when the IMFP and SEP of the reference material and the IMFP of the sample are known [3–5], indicating that the obtained SEP strongly depends on the IMFP of the reference material and the sample and the predictive equation used for the SEP correction of the reference material. The EPES analysis without the reference material can be performed if the elastic peak intensity is measured in absolute units, but the IMFP is required for the determination of the SEP by the absolute EPES analysis [1].

Another experimental approach for determining the SEP is the REELS analysis [6–12]. The REELS analysis for determining the SEP does not require a reference material, but the IMFP of the sample should be known, indicating that the derived SEP depends on the IMFP used in the analysis. Recently, a procedure for determining the DIMFP and DSEP simultaneously by the background analysis of two REELS spectra using the elastic cross section and an estimate for the IMFP as input parameters has been proposed [25]. The authors have also been involved in the study on the interaction of electrons with the solid surface [26–30], and recently proposed an analytical approach to determine simultaneously the IMFP, SEP, and DSEP in absolute units from an absolute REELS spectrum [31,32]. The proposed approach requires only the elastic scattering cross section and the normalized DIMFP as input parameters in the analysis. The proposed approach was applied to Ni [31–33] and Au [34] and found to be effective to the experimental determination of the IMFP, SEP and DSEP.

With respect to theoretical approaches to understanding the interaction of electrons with the solid surface, theoretical studies based on the dielectric response of solids to external charged particles has been intensively performed [26,35–38]. Another powerful theoretical approach for understanding the interaction of electrons with the solid surface is Monte Carlo (MC) simulation of an electron spectrum. However, most of MC simulations of electron spectra do not take into account the surface excitation [37]. The authors investigated simple MC modeling of a REELS spectrum by taking into consideration energy loss processes due to surface excitations as well as bulk excitations [33,39]. In the developed MC simulation, the IMFP, SEP and DSEP determined by the absolute REELS analysis can be used for describing the inelastic interaction of electrons with solids, and it is found that the developed MC simulation can trace the experimental absolute REELS spectra very well.

In the present paper, the results of the investigation of the inelastic interaction of 300–3000 eV electrons with the Ni and Au surfaces using the analytical approach proposed by the authors will be described. The MC modeling of a REELS spectrum, the application of the experimentally determined SEP, DSEP and IMFP to the MC simulation, and the results of the MC simulation will also be described.

2. Experiment

All experiments were performed using a noble cylindrical mirror analyzer (CMA) developed by one of the authors (K.G.) [40]. The CMA is equipped with a Faraday cup as a detector of signal electrons, and provides the absolute electron current as a signal. The detection angle of the CMA was $42.3^\circ \pm 6^\circ$. The energy resolution of the CMA was 0.25%. The transmission function of the CMA used for the correction of the intensity of spectra was measured by the transmission of light [1]. The measured value of the transmission efficiency of the CMA mesh is in good agreement with the efficiency calculated from the size of the mesh. The samples used in the present study were polycrystalline Ni and Au, and their surfaces were sputter cleaned using 250–300 eV Ar^+ ions. The base pressure of the apparatus was 2×10^{-8} Pa. The primary energy of electrons for the REELS measurement was varied from 300 to 3000 eV. The beam current of primary electrons was 1 μA for all measurements. Details of the experimental setup are described elsewhere [1].

3. REELS analysis

In the present analytical approach, the IMFP, SEP and DSEP are simultaneously determined from an absolute REELS spectrum. The present approach is based on the Landau theory [41], which originally describes energy losses of electrons during transport in solids under the assumption that changes in the electron direction of motion can be neglected. Similar procedure has been intensively studied [6–9,42,43]. The Landau theory can be extended by taking into account angular deflections of moving electrons by elastic scattering and energy losses by surface excitations, and is rewritten as [31,32]:

$$J(s) = F(s)\sum_{m=0}^{\infty}\alpha_m[\lambda_b K_b(s)]^m \sum_{l=0}^{\infty} P_s^{\text{total},l}\left[\frac{K_s^{\text{in}}(s)}{P_s^{\text{in}}}\right]^l \quad (1)$$

where $J(s)$ and $F(s)$ are the Fourier transforms of a measured REELS spectrum; $J(E)$ and the energy distribution of primary electrons $F(E)$. s is the Fourier parameter conjugate to the energy E. The first and second $\sum$ terms with respect to the summation over m and l describe the transport of electrons in the bulk and energy loss processes by surface excitations, respectively. m is the number of bulk excitation events undergone by signal electrons during transport in the solid. α_m is the probability that primary electrons experience m-fold bulk excitation events in the solid before being emitted from the surface. λ_b is the IMFP and $K_b(s)$ is the Fourier transform of the DIMFP, $K_b(\Delta E)$, and they satisfies the following equation:

$$1 = \lambda_b \int_0^{E_0} K_b(\Delta E)\,\mathrm{d}(\Delta E) \quad (2)$$

where E_0 is the primary energy of electrons.

l in the second $\sum$ term is the number of surface excitation events and $P_s^{\text{total},l}$ is the probability that electrons participate in l-fold surface excitation events. $K_s^{\text{in}}(s)$ is the Fourier transform of the DSEP $K_s^{\text{in}}(\Delta E)$ for incoming electrons. P_s^{in} is the SEP for incoming electrons and satisfies the following equation with DSEP:

$$1 = (P_s^{\text{in}})^{-1} \int_0^{\infty} K_s^{\text{in}}(\Delta E)\ \mathrm{d}(\Delta E) \quad (3)$$

For the analysis of the REELS spectrum in absolute units, the REELS spectrum is self-consistently deconvoluted into components relevant to electrons participating in m-fold bulk ($m = 0, 1, 2, \ldots$) and l-fold surface ($l = 0, 1, 2, \ldots$) excitation events according to Eq. (1). A REELS spectrum $J(E)$ is obtained by correcting the intensity of the measured REELS spectrum by the transmission function. The energy distribution of primary electrons $F(E)$ is taken from the elastic peak of the relevant REELS spectrum. The DIMFP $K_b(\Delta E)$ is calculated using the dielectric response theory [44] with the Pen's algorithm [45] based on the Ritchie–Howie algorithm [46] for the extension of the ω-dependent energy loss function to the momentum-energy