Surface Science 620 (2014) 17–22

Contents lists available at ScienceDirect

Surface Science

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

Determination of the Cu 2p primary excitation spectra for Cu, Cu_2O and CuO

N. Pauly [a,*], S. Tougaard [b], F. Yubero [c]

[a] Université Libre de Bruxelles, Service de Métrologie Nucléaire (CP 165/84), 50 av. F. D. Roosevelt, B-1050 Brussels, Belgium
[b] Department of Physics, Chemistry and Pharmacy, University of Southern Denmark, DK-5230 Odense M, Denmark
[c] Instituto de Ciencia de Materiales de Sevilla, Univ. Sevilla - CSIC, av. Américo Vespucio 49, E-41092 Sevilla, Spain

ARTICLE INFO

Article history:
Received 30 July 2013
Accepted 10 October 2013
Available online 17 October 2013

Keywords:
XPS, Photoelectron spectroscopy
Core-hole effect, surface effect
Copper, copper oxide

ABSTRACT

The shape and intensity of photoelectron peaks are strongly affected by extrinsic excitations due to electron transport out of the surface (including bulk and surface effects) and to intrinsic excitations due to the sudden creation of the static core hole. These effects must be included in the theoretical description of the emitted photoelectron spectra. We have calculated the effective energy-differential inelastic electron scattering cross section for XPS, including both surface and core hole effects, within the dielectric response theory by means of the QUEELS-XPS software (QUantitative analysis of Electron Energy Losses at Surfaces for XPS). The full XPS spectrum is then modeled by convoluting this energy loss cross section with the primary excitation spectrum that accounts for all effects which are part of the initial photo-excitation process, i.e. lifetime broadening, spin–orbit coupling, and multiplet splitting. The shape of this primary excitation spectrum is determined by requiring close agreement between the resulting theoretical spectrum and the experimental XPS spectrum. These calculations were performed for Cu 2p peaks of Cu, Cu_2O, and CuO. For CuO, we compare the obtained primary excitation spectra with first principle calculations performed with the CTM4XAS software (Charge Transfer Multiplet program for X-ray Absorption Spectroscopy) for the corresponding emissions and we find good quantitative agreement.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is currently the most heavily used analytical techniques to obtain information about composition, electronic structure and chemical information at solid surfaces [1]. To extract quantitative information on surface atomic concentrations and on chemical bonds, it is necessary to account for the high background intensity of inelastically scattered electrons which is superimposed on the primary excited peaks. Several methods have been suggested to subtract this inelastic background from the initial spectrum. Among these, Shirley [2], Tougaard [3] and straight line [4] methods are in practice the most commonly used procedures.

The energy loss processes responsible for the background have two origins, namely the "intrinsic" and "extrinsic" excitations [5,6]. Intrinsic excitations are due to the sudden creation of the static core-hole and to the associated electric field that excites valence electrons and thus results in an energy loss by the photoelectron. Extrinsic excitations take place during the photoelectron transport process and are due to the time and space varying electric field from the moving photoelectron which also causes excitations and thereby energy losses. We note that such processes occur when the electron travels not only in the medium but also in the vacuum where the photoelectron interacts with its image charge. Thus extrinsic excitations are themselves generally separated into bulk (occurring in the medium considered as infinite) and surface processes (occurring while the electron is moving in a shallow region in the medium and in the vacuum). However, such strict separation between the various processes is not exactly valid because the effects interfere [7] and a one-step model is necessary for an accurate description.

Such one-step model based on a semi-classical dielectric response model has been proposed [7,8] and implemented in the user-friendly QUEELS-XPS software (QUantitative analysis of Electron Energy Losses at Surfaces for XPS) [9,10] which determines the energy-differential inelastic electron scattering cross-sections for XPS, K_{sc}^{XPS}, including bulk, surface and core hole effects as well as interference between these effects. This model was previously tested [8,11–13] and was shown to give a good quantitative description of the energy and angular dependence of the loss structure for various photoelectron emissions from metallic aluminium, silicon, metallic copper and iron.

In these papers, the full XPS spectra are modeled by convoluting the calculated energy loss cross section, K_{sc}^{XPS} with the primary excitation spectrum, $F(E)$ which accounts for all effects that are part of the initial photo-excitation process like life time broadening, spin–orbit coupling

* Corresponding author. Tel.: +32 2 6502083; fax: +32 2 6504534.
E-mail address: nipauly@ulb.ac.be (N. Pauly).

0039-6028/$ – see front matter © 2013 Elsevier B.V. All rights reserved.
http://dx.doi.org/10.1016/j.susc.2013.10.009

and multiplet splitting and this *F(E)* is considered as an input in the calculations. The primary goal of these previous works was to test the ability of the model to quantitatively account for observed changes in the experimental spectra when changing experimental parameters such as the excitation energy and angle of emission. It was found that this dielectric response model gave a good quantitative description. In the present work, we focus on determination of the primary excitation spectrum *F(E)* from measured photoelectron spectra.

We have thus calculated in this paper Cu 2p primary excitation spectra of Cu, Cu_2O and CuO. These metallic and oxidized forms of copper have been chosen for two reasons. First, copper is applied in a wide variety of disciplines. In its metallic form, it is always a material of choice for a variety of domestic, industrial and high-technology applications. As for copper oxides, in particular cupric (CuO) and cuprous (Cu_2O) oxide, they are of considerable interest for a multitude of applications as gas sensors, magnetic storage and recently high-T_c superconductors [14]. Second, Cu_2O and CuO display interesting and characteristic electronic structures (closed d10 shell in the case of Cu_2O and open d9 shell for CuO) due to the influence of electron-correlation effects; this results in very different Cu 2p photoemitted signals [15]. It is thus of particular interest to accurately determine the primary excitation spectra of these materials.

In the following section we describe the model used in the QUEELS-XPS software as well as the procedure followed to obtain the primary excitation spectra of the chosen transitions. Results of *F(E)* obtained within the method will then be discussed and compared, when possible, with theoretical calculations generated with the CTM4XAS software (Charge Transfer Multiplet program for X-ray Absorption Spectroscopy) [16].

2. Theoretical model

1. QUEELS formalism

The software package QUEELS-XPS [9,10] implements the dielectric response model [7] describing the interactions of electrons with semi-infinite media in terms of the dielectric properties of the bulk material and incorporates the effects of the surface, of the static core hole created during the photoionization process, and excitations in the vacuum after the photoelectron has left the surface, as well as interference between these effects. As the principles of this XPS formalism are abundantly described in the literature [6–8], we only describe here the basic elements of the model.

We consider the case of an electron-hole pair created at a depth x_0 below the surface of a semi-infinite medium characterized by its dielectric function $\varepsilon(\mathbf{k},\omega)$. The electron emission is the consequence of the photon energy absorption of a core electron. The electron travels along a straight line with velocity v, energy E and angle θ with respect to the surface normal, while the core hole is stationary with infinite lifetime. Within this model, the effective inelastic electron scattering cross section $K_{eff}^{XPS}(E,\hbar\omega,x_0,\theta)$ is defined as the average probability that the electron, excited at depth x_0, loses an energy $\hbar\omega$ per unit energy loss and per unit path length traveled inside the solid (the *XPS* in the expression of K_{eff} distinguishes this from the similar expression valid for REELS experiment where the influence of the core hole is absent [17]).

$K_{eff}^{XPS}(E,\hbar\omega,x_0,\theta)$ is then expressed in terms of the induced potential $\Phi_{ind}(\mathbf{k},\omega)$ created by the static hole and the moving electron [7]:

$$K_{eff}^{XPS}(E,\hbar\omega,x_0,\theta)=\frac{2}{(2\pi)^4 x_0\hbar^2\omega}\int_{-\infty}^{+\infty}dt\int d\mathbf{r}\rho_e(\mathbf{r},t)\times \mathrm{Re}\left[i\int d\mathbf{k}\,\mathbf{kv}\Phi_{ind}(\mathbf{k},\omega)e^{i(\mathbf{kr}-\omega t)}\right], \quad (1)$$

where $\mathbf{k}$ is the transferred momentum, $\mathbf{r}$ is the electron position, $\rho_e(\mathbf{r},t)$ is the charge density of the electron, t is the time (at $t=0$ photoexcitation occured), and Re[] refers to the real part of the quantity in brackets. $\Phi_{ind}(\mathbf{k},\omega)$ is obtained within the surface reflection model [18] in which the potential of a system of moving charges in a semi-infinite medium is obtained by considering two infinite pseudomedia, the medium (M) and the vacuum (V). In the pseudomedia M and V, we have to consider all charges and their images. For XPS, at $t>0$, the relevant charges are the electron $\rho_e=-e\delta(\mathbf{r}-\mathbf{x}_0-\mathbf{v}t)$, the core hole $\rho_h=e\delta(\mathbf{r}-\mathbf{x}_0)$, their images $\rho_{e^i}=-e\delta\left(\mathbf{r}+\mathbf{x}_0-\mathbf{v}^i t\right)$, $\rho_{h^i}=e\delta(\mathbf{r}+\mathbf{x}_0)$ and fictitious surface charges σ_M and σ_V introduced to satisfy the boundary conditions (in these expressions, $\mathbf{x}_0=(-x_0,0,0)$). We note that fictitious surface charges are determined by the requirement that the potentials, and the normal components of the displacement vectors in each pseudomedium must be continuous at the surface. Then, solution of Poisson's equation in Fourier space for each of the two infinite pseudomedia allows to obtain the induced potentials Φ_{ind}^M and Φ_{ind}^V. The detailed final expressions for K_{eff}^{XPS} are given in Ref. [7].

To perform this calculation, it is necessary to know the dielectric function of the medium $(\mathbf{k},\omega)$ or equivalently the energy loss function (ELF) $\mathrm{Im}\{-1/(\mathbf{k},\omega)\}$. The ELF is thus the only input in the calculations. To evaluate this latter, we consider as a model the expansion in Drude–Lindhard type oscillators [19]

$$\mathrm{Im}\left\{-\frac{1}{\varepsilon(\mathbf{k},\omega)}\right\}=\sum_{i=1}^{n}\frac{A_i\hbar\gamma_i\hbar\omega}{\left(\hbar^2\omega_{0ik}^2-\hbar^2\omega^2\right)^2+\hbar^2\gamma_i^2\hbar^2\omega^2}\theta(\hbar\omega-E_G) \quad (2)$$

with the dispersion relation:

$$\hbar\omega_{0ik}=\hbar\omega_{0i}+\alpha_i\frac{\hbar^2k^2}{2m}. \quad (3)$$

A_i, $\hbar\gamma_i$, $\hbar\omega_{0ik}$ and α_i are the strength, width, energy and dispersion of the ith oscillator, respectively and the step function $\theta(\hbar\omega-E_G)$ is included to describe the effect of the energy band gap E_G present in semiconductors and insulators. The parameters in the expansion are taken from Ref. [20] for the materials studied in this work, namely, Cu, Cu_2O and CuO.

In XPS experiments, electrons from a wide range of depths are sampled. This implies to perform a weighted average of K_{eff}^{XPS} over the total of all path lengths x [7] with the weight function $Q(E,x,\theta)$ which is the path-length distribution function for those electrons that have undergone a single inelastic collision. The result is the inelastic scattering cross-section

$$K_{sc}^{XPS}(E,\hbar\omega,\theta)=\frac{\int_0^\infty dxQ(E,x,\theta)K_{eff}^{XPS}(E,\hbar\omega,x_0,\theta)}{\int_0^\infty dxQ(E,x,\theta)}. \quad (4)$$

Within this model, K_{sc}^{XPS} includes bulk, surface and core hole effects as well as interferences between these effects.

We show in Fig. 1 the resulting effective inelastic electron scattering cross sections K_{eff}^{XPS} and the inelastic scattering cross-section K_{sc}^{XPS} obtained for photoelectrons of 320 eV emitted at an angle $\theta=15°$ with respect to the surface normal from a copper sample. For K_{eff}^{XPS}, we have chosen to show spectra from 7 emission depths, namely, 1, 2, 5, 10, 20, 40 and 65 Å. This example has been chosen because it corresponds to one of the cases studied in this paper (Cu $2p_{3/2}$ photoelectron excited by a Mg K_α X-ray source).

2. Theoretical description of the XPS spectra

An XPS spectrum can be seen as the addition of the contribution from electrons that have undergone an increasing number of energy