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Quantitative analysis of Ni 2p photoemission in NiO and Ni diluted in a SiO_2 matrix

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ABSTRACT

In X-ray excited photoelectron emission (XPS), besides the initial excitation process, 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. To make an accurate quantitative interpretation of features observed in XPS, these effects must be included in the theoretical description of the emitted photoelectron spectra. It was previously shown [N. Pauly, S. Tougaard, F. Yubero, Surf. Sci. 620 (2014) 17] that these three effects can be calculated by means of the QUEELS-XPS software (QUantitative analysis of Electron Energy Losses at Surfaces for XPS) in terms of effective energy-differential inelastic electron scattering cross-sections. The only input needed to calculate these cross-sections is the energy loss function of the media which is determined from analysis of Reflection Electron Energy Loss Spectra (REELS). 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. In this paper we apply the previously presented procedure to the study of Ni 2p photoemission in NiO and Ni diluted in a SiO_2 matrix (Ni:SiO_2), samples being prepared by reactive magnetron sputtering at room temperature. We observe a significant difference between the corresponding Ni 2p primary excitation spectra. The procedure allows quantifying the relative intensity of the $c3d^9L$, $c3d^{10}L^2$, and $c3d^8$ final states contributing to the Ni 2p photoemission spectra of the Ni^{2+} species in the oxide matrices. Especially, the intensity ratio in NiO between the non-local and local contributions to the $3d^9L$ configuration is determined to be 2.5. Moreover the relative intensity ratio of the $c3d^9L/c3d^{10}L^2/c3d^8$ configurations is found to be 1.0/0.83/0.11 for both the NiO and Ni:SiO_2 samples.

1. Introduction

X-ray photoelectron spectroscopy (XPS) is currently extensively used to obtain information about the composition and the electronic structure of atoms in the surface region of materials [1]. XPS spectra consist of the energy distribution of emitted photoelectrons after excitation by X-ray absorption and electron transport out of the solid. For accurate spectrum analysis, it is necessary to have a quantitative understanding of energy loss processes and elastic scattering events experienced by the photoelectrons during their transport out of the solid.

Quite often, only a qualitative comparison between experimental results and theoretical simulations of XPS spectra can be done due to the fact that the inelastic background of the experimental data is treated based on linear or Shirley type background subtraction [2], methods that do not rely on a quantitative description of the energy loss processes which have a strong influence on the shape and intensity of the measured photoemitted peaks.

A one-step model based on a semi-classical dielectric response description has been proposed [3,4] and implemented in the QUantitative analysis of Electron Energy Losses at Surfaces for XPS software (QUEELS-XPS) [5], which determines the energy-differential inelastic electron scattering cross-sections for XPS, K_{sc}^{XPS}, including bulk, surface and core hole induced losses as well as interference between them. By comparison to the experiments, this has been shown [6] to give a good quantitative description of the energy and angular dependence of the loss structure for various photoelectron emissions from several materials. Besides, based on the QUEELS-XPS description of the electron energy losses, a method was recently proposed [9] which allows to directly determine the primary excited spectrum $F(E)$ (which accounts for all contributions that are part of the initial photoexcitation process like lifetime broadening, spin–orbit coupling and multiplet splitting) from a measured experimental XPS spectrum simply by using the K_{sc}^{XPS} cross-section in the Tougaard background.

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In the present paper we apply this method to determine the Ni 2p primary excitation spectra of NiO and Ni diluted in a SiO_2 matrix (Ni:SiO_2) from the corresponding experimental Ni 2p photoemitted signal. These systems have been selected because in the past, interpretation of the spectral line shape of the Ni 2p photoemission of Ni^{2+} compounds has been the subject of intense experimental and theoretical works [10–16]. In this work we use the QUEELS-XPS cross-section to quantitatively isolate the primary excited Ni 2p spectrum which can directly be compared with theoretical calculations.

2. Experimental details

NiO and Ni:SiO_2 samples were prepared by reactive magnetron sputtering at room temperature. A gas mixture Ar/O_2 at a total pressure of 5×10^{-3} mbar was used to produce the magnetron discharge. Ar and O_2 were dosed by mass flow controllers, with a relative flow rate ϕ (Ar)/ ϕ (O_2) of 10/1. The distance between the magnetron target and the substrate was 10 cm. NiO samples were prepared from a pure Ni target. Ni:SiO_2 samples were prepared from a Si target with a Ni stripe (2 mm width) wrapped to it. Polished Si wafers were used as substrates for the film deposition. Elemental depth profiles were evaluated by Rutherford backscattering spectrometry (RBS) using an ~2.0 MeV He^{2+} beam and a passivated implanted planar silicon detector located at a 165° scattering angle in a 3 MV tandem accelerator (CNA, Seville, Spain). Analysis was done using a SIMNRA code [17] and the concentration depth distribution of Ni within the SiO_2 matrix was found to be homogeneous. More details can be found elsewhere [18,19].

REELS measurements were performed using primary electron energies of 500, 1000 and 2000 eV for NiO and 500 eV for Ni:SiO_2. The incidence and exit angles of the electron beam were at 60° and 0° to the surface normal respectively. The energy resolution of these measurements was about 0.8 eV as determined by the full width at half maximum of the corresponding elastic peaks.

XPS characterization was done with a monochromatized Al Ka X-ray source irradiating the sample at an angle of 54° to the surface normal. Spectra were measured normal to the surface with a PHOIBOS150 electron spectrometer. A pass energy of 10 eV was chosen to enhance the energy resolution.

3. Dielectric function of NiO and Ni:SiO_2

The starting point of this study is the determination of the complex dielectric function $\varepsilon(k,\omega)$, or equivalently the energy loss function (ELF) $\mathrm{Im}\{-1/\varepsilon(k,\omega)\}$, of the considered materials since this is the only input in the QUEELS-XPS analysis. This is determined from analysis of REELS experiments [20]. The basic idea of the procedure is to use theory to simulate a REELS cross-section based on a model ELF. By the constraint that this must fit with an experimental REELS cross-section, $\mathrm{Im}\{-1/\varepsilon(k,\omega)\}$ can thus be determined. To enhance the accuracy of the determined ELF, the theory is usually compared to experimental REELS recorded at different primary energies.

As a first step we have to remove multiple scattering contributions from the measured REELS spectra in order to obtain the normalized experimental inelastic scattering cross-section $\lambda K_{exp}(E, \hbar\omega, \theta_i, \theta_o)$, where λ is the corresponding inelastic mean free path (E, θ_i and θ_o being the energy, the entrance angle and the exit angle – measured with respect to the surface normal – of the moving electron, respectively). This is done with the method of Tougaard and Chorkendorff [21] implemented in the software QUASES-XS-REELS (Quantitative Analysis of Surface Electron Spectra Cross Sections determined by Reflection Electron Energy Loss Spectroscopy) [22]. The resulting K_{exp} is an effective cross-section which includes surface and bulk excitations and, as pointed out in the paper by Tougaard and Chorkendorff [21] and later by others [23], it can contain erroneous contributions from double surface and mixed surface and bulk excitations. These effects are however usually negligible since it has been found in numerous studies that the cross-sections are in agreement with the calculated theoretical single scattering cross-sections of the surface and bulk contributions (see e.g. Refs. [24–26] and references therein).

Next, this experimental cross-section K_{exp} is compared to the theoretical cross-section K_{sc} calculated by the semi-classical dielectric response model of Yubero and Tougaard [27]. This model, including bulk and surface excitations as well as interference between them, allows to obtain the differential inelastic electron scattering cross-section spectrum $K_{sc}(E, \hbar\omega, \theta_i, \theta_o)$ in REELS for an electron of energy E interacting with a solid and following a V-type trajectory making an angle θ_i at the entrance and θ_o at the exit. The complete theory of the model has been described in detail in Ref. [28], its validity has been experimentally demonstrated in several papers (see Ref. [24], for instance) and the accuracy of the V-type trajectory assumption has been theoretically evaluated in Ref. [29]. The model has been implemented into a user-friendly software package, namely QUEELS-$\varepsilon(k,\omega)$-REELS, which is generally available [30].

To determine K_{sc}, the only required input in QUEELS-$\varepsilon(k,\omega)$-REELS is the dielectric function $\varepsilon(k,\omega)$ or more exactly the ELF, $\mathrm{Im}\{-1/\varepsilon(k,\omega)\}$, of the medium. To evaluate the ELF, we consider as a model the expansion in Drude–Lindhard type oscillators [31]

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

with the dispersion relation:

$$\hbar\omega_{0ik} = \hbar\omega_{0i} + \alpha_i \frac{\hbar^2 k^2}{2m}. \tag{2}$$

In these expressions, A_i, $\hbar\gamma_i$, $\hbar\omega_{0ik}$ and a_i denote the strength, width, energy and dispersion of the ith oscillator, respectively while E_G is the band gap energy. 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 oscillator strengths are adjusted to fulfill the optical sum rule [32].

In the ELF determination procedure, the parameters A_i, $\hbar\gamma_i$, $\hbar\omega_{0ik}$, and a_i of Eqs. (1) and (2) are varied until good agreement between the calculated, K_{sc}, and experimental differential inelastic scattering cross-sections, K_{exp}, is obtained (for all primary electron energies considered). E_G is taken from the literature. This procedure allows to obtain accurate ELF and has been successfully used in the past to determine $\varepsilon(k,\omega)$ for many materials (see Refs. [24–26] for instance).

Fig. 1 shows the results of the fitting procedure for NiO to REELS cross-sections obtained at the three primary electron energies, $E =$ 500, 1000 and 2000 eV with a fixed angular configuration of $\theta_i = 60°$ and $\theta_o = 0°$. The parameters of the ELF determined in this way are shown in Table 1. The value of the band gap energy, $E_G = 3.7$ eV, is taken from Ref. [33] supplied by the National Institute of Standards and Technology (NIST). The values of the dispersion parameters a_i are related to the effective mass of the electron. The best fit for all energies was obtained with $a_i = 0.2$ for the excitations related to the valence band electrons and $a_i = 0.02$ for the oscillators due to transitions involving the Ni 3p electrons. These values are consistent with previously found values for wide band gap semiconductors [25,26,30]. As can be seen in Fig. 1, this gives a good agreement with the experiment at all primary energies.

For small energy losses ($\hbar\omega < 50$ eV), the energy positions of structures in the experimental REELS have been compared with theoretical calculations for NiO (see Ref. [34] for instance and references therein). The energy positions of structures in the quantitative ELF obtained from the present procedure corresponds well with these previous results. The ELF is dominated by one broad feature at 23.1 eV corresponding to the bulk plasmon. Two other large features are also observed at 8 and 38 eV, corresponding to O 2p$\sigma \rightarrow$ Ni 3d and O 2 s $\rightarrow$ Ni 3d transitions. The quite large oscillator at 14.5 eV could be ascribed to the O