Quantitative analysis of Ni 2p photoemission in NiO and Ni diluted in a SiO2 matrix

Pauly, N.; Yubero, F.; García-García, F J; Tougaard, Sven Mosbæk

Published in:
Surface Science

DOI:
10.1016/j.susc.2015.09.012

Publication date:
2016

Document version
Final published version

Citation for published version (APA):
Quantitative analysis of Ni 2p photoemission in NiO and Ni diluted in a SiO2 matrix

N. Pauly a,⁎, F. Yubero b, F.J. García-García b, S. Tougaard c

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

A R T I C L E   I N F O

Article history:
Received 18 June 2015
Accepted 12 September 2015
Available online 21 September 2015

Keywords:
XPS
Photoelectron spectroscopy
Non-local screening effect
Core-hole effect
Surface effect
Nickel oxide

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 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 SiO2 matrix (Ni:SiO2), 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 c3d9L3L2, c3d10L2, and c3d8 final states contributing to the Ni 2p photoemission spectra of the Ni2+ species in the oxide matrices. Especially, the intensity ratio in NiO between the non-local and local contributions to the c3dL configuration is determined to be 2.5. Moreover the relative intensity ratio of the c3d9L/c3d10L/c3d8 configurations is found to be 1.0/0.83/0.11 for both the NiO and Ni:SiO2 samples.

© 2015 Elsevier B.V. All rights reserved.

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 (QUEELS-XPS) [5], which determines the energy–differential inelastic electron scattering cross-sections for XPS, K XS, 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 XS cross-section in the Tougaard background.
In the present paper we apply this method to determine the Ni 2p primary excitation spectra of NiO and Ni diluted in a SiO2 matrix (Ni-SiO2) 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 Ni2+ 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-SiO2 samples were prepared by reactive magnetron sputtering at room temperature. A gas mixture Ar/O2 at a total pressure of 5 × 10−3 mbar was used to produce the magnetron discharge. Ar and O2 were dosed by mass flow controllers, with a relative flow rate φ(Ar)/φ(O2) 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-SiO2 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 a Rutherford backscattering spectrometry (RBS) using an ~2.0 MeV He2+ 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 SiO2 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-SiO2. 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 Kα X-ray source irradiating the sample at an angle of 54° to the surface normal. Spectra were measured normal to the surface with a PHIIBOS150 electron spectrometer. A pass energy of 10 eV was chosen to enhance the energy resolution.

3. Dielectric function of NiO and Ni-SiO2

The starting point of this study is the determination of the complex dielectric function ε(k,ω), or equivalently the energy loss function (ELF) Im[−1/ε(k,ω)], 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, Im[−1/ε(k,ω)] 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 Kexp(E, hω, θo, θi), where λ is the corresponding inelastic mean free path (E, θi, and θo 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 Kexp 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 Kexp is compared to the theoretical cross-section Kth 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 Kth(E, hω, θo, θi) in REELS for an electron of energy E interacting with a solid and following a V-type trajectory making an angle θi at the entrance and θo 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-ε(κ,ω)-REELS, which is generally available [30].

To determine Kth, the only required input in QUEELS-ε(κ,ω)-REELS is the dielectric function ε(κ,ω) or more exactly the ELF, Im[−1/ε(κ,ω)], of the medium. To evaluate the ELF, we consider as a model the expansion in Drude–Lindhard type oscillators [31]

\[ \text{Im} \left\{ \frac{1}{\varepsilon(k,\omega)} \right\} = \sum_{i=1}^{n} \frac{\varepsilon_i}{\omega_i^2 - \omega^2 + \varepsilon_i^2} = \sum_{i=1}^{n} A_i \gamma_i \frac{\omega}{\omega^2 + \varepsilon_i^2} \]

with the dispersion relation:

\[ \omega_{\text{cka}} = \omega_{\text{ca}} + \alpha \frac{\hbar^2 k^2}{2m} \]

In these expressions, Ai, γi, ωcka and ai denote the strength, width, energy and dispersion of the ith oscillator, respectively while Ec is the band gap energy. The step function θ(ωo − Ec) is included to describe the effect of the energy band gap Ec present in semiconductors and insulators. The oscillator strengths are adjusted to fulfill the optical sum rule [32].

In the ELF determination procedure, the parameters Ai, γi, ωcka, and ai of Eqs. (1) and (2) are varied until good agreement between the calculated, Kcal, and experimental differential inelastic scattering cross-sections, Kexp, is obtained (for all primary electron energies considered). Ec is taken from the literature. This procedure allows to obtain accurate ELF and has been successfully used in the past to determine ε(κ,ω) 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 θo = 60° and θi = 0°. The parameters of the ELF determined in this way are shown in Table 1. The value of the band gap energy, Ec = 3.7 eV, is taken from Ref. [33] supplied by the National Institute of Standards and Technology (NIST). The values of the dispersion parameters ai are related to the effective mass of the electron. The best fit for all energies was obtained with ai = 0.2 for the excitations related to the valence band electrons and ai = 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 (hω < 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 2pσ → Ni 3d and O 2 s → Ni 3d transitions. The quite large oscillator at 14.5 eV could be ascribed to the O
Ni 4p, O 2p \rightarrow Ni 4s or Ni 3d \rightarrow Ni 4p transitions. For energy loss 50 eV, less precise data exist in the literature, but our result agrees well with ELF reconstructed from X-ray scattering factors (a complete database can be found in Ref. [35]). Moreover, the narrow oscillators at 66.3 and 69.2 eV correspond to excitations of Ni 3p electrons to unoccupied states near the Fermi level $E_F$.

For the Ni:SiO$_2$ sample, it was found by XPS that the Ni content within the SiO$_2$ matrix was about 5%. It is therefore expected that the dielectric description of the medium where the electrons are traveling is to a good approximation equal to that of SiO$_2$ which was determined previously [36]. The comparison between them is excellent proving that the SiO$_2$ ELF can be used to describe the dielectric properties of Ni:SiO$_2$. We report in Table 1 the ELF parameters of SiO$_2$. SiO$_2$ is characterized by a single broad plasmon peak at 23.1 eV and a large band gap ($E_g = 9.3$ eV).

Fig. 3 shows the determined ELF of NiO corresponding to the values in Table 1 together with the ELF previously reported for SiO$_2$ [36], and thus valid also for Ni:SiO$_2$.

### 4. Scattering cross-section for XPS of NiO and Ni:SiO$_2$

Also based on the semi-classical dielectric response theory, a model has been proposed [3,4] to be applied to an XPS configuration, including now both a moving photoelectron and a static core hole created during the photoemission process and responsible for intrinsic excitations. This model allows to determine the energy-differential inelastic electron single scattering cross-sections for XPS, $K_{SC}^{XPS}(E, \hbar \omega, \theta)$ (where $\theta$ is the electron emission angle), including bulk, surface and core hole effects as well as interference between these effects. It has been implemented in the user-friendly QUEELS-XPS software (QUantitative analysis of Electron Energy Losses at Surfaces for XPS) [5]. As for the QUEELS-$\epsilon(k,\omega)$-REELS software described above, the ELF of the material is the only input in the calculations (see full description of the model in Ref. [3]).

Thus, based on the ELFs obtained from analysis of REELS in Section 3, we obtain, as shown in Fig. 4, the differential inelastic single scattering cross-section, $K_{SC}^{XPS}$, for photoelectrons of 630 eV energy emitted perpendicular to the surface from NiO and Ni:SiO$_2$, respectively. This configuration has been chosen because it corresponds to the cases studied in this paper (Ni 2p photoelectrons excited by an Al Ka X-ray source).

### 5. Analysis of Ni 2p photoelectron emission

An experimental XPS spectrum $I(E)$ can be seen as the addition of the contributions from electrons that have undergone an increasing number of energy loss events [37] and can thus be reproduced by the multiple convolution of a primary excitation function $F(E)$, considered

---

**Table 1** Parameters used to model the dielectric loss function of NiO. The SiO$_2$ data are taken from Ref. [36].

<table>
<thead>
<tr>
<th>Medium</th>
<th>$i$</th>
<th>$\hbar \omega_0$ (eV)</th>
<th>$A_i$ ($\hbar^3$)</th>
<th>$\hbar \gamma_i$ (eV)</th>
<th>$a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO</td>
<td>1</td>
<td>8.0</td>
<td>3.74</td>
<td>5.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>14.5</td>
<td>5.55</td>
<td>8.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>23.1</td>
<td>246.50</td>
<td>11.5</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>38.0</td>
<td>236.71</td>
<td>16.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>52.0</td>
<td>103.68</td>
<td>20.0</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>6</td>
<td>66.3</td>
<td>11.85</td>
<td>2.0</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>69.2</td>
<td>11.85</td>
<td>2.0</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>8</td>
<td>85.0</td>
<td>257.58</td>
<td>40.0</td>
<td>0.02</td>
</tr>
<tr>
<td>SiO$_2$</td>
<td>1</td>
<td>15.0</td>
<td>7.82</td>
<td>5.0</td>
<td>0.02</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>23.1</td>
<td>277.91</td>
<td>14.0</td>
<td>0.02</td>
</tr>
</tbody>
</table>

---

**Fig. 1.** Comparison of the normalized inelastic cross-sections $\lambda K$ for NiO obtained from REELS experiments (solid line) using QUASES-XS-REELS and from the best fit result (dashed line) evaluated using $\epsilon(k\omega)$ from Table 1 and QUEELS-$\epsilon(k,\omega)$-REELS for incident electrons on NiO with energies of 500, 1000 and 2000 eV.

**Fig. 2.** Comparison of the normalized inelastic cross-sections $\lambda K$ obtained from REELS experiment (solid line) using QUASES-XS-REELS and from QUEELS-$\epsilon(k,\omega)$-REELS (dashed line) with the SiO$_2$ ELF (see Table 1) for electron with $E = 500$ eV incident on Ni:SiO$_2$. 

---

N. Pauly et al. / Surface Science 644 (2016) 46–52
as an input parameter, with the energy-differential single inelastic scattering cross-section, $K_{sc}^{XPS}$, such as

$$f(E) = f(E) + \lambda_{sc} \int_{E}^{E'} F(E')K_{sc}^{XPS}(E, E'-E)dE' + \sum_{n=2}^{\infty} J_n$$  \hspace{1cm} (3)

where $K_{sc}^{XPS}$ is the inelastic single scattering cross-section as defined above for an energy loss $E'$—$E$ evaluated for electrons with kinetic energy $E$, and $\lambda_{sc}$ is the inelastic scattering mean free path defined as

$$\lambda_{sc}(E, \theta) = \left[ \int_{0}^{\infty} K_{sc}^{XPS}(E, \hbar\omega, \theta)d\omega \right]^{-1}.$$  \hspace{1cm} (4)

The last term in Eq. (3) describes the contribution from multiple scattered electrons to the spectrum: $J_0(E)$ is the double scattering contribution, $J_1(E)$ the triple scattering contribution, and so on. $f(E)$ is thus modeled by repeated convolution, accounting for multiple losses.

Note that in previous expression (Eq. (3)), we have considered $K_{sc}^{XPS}$ not only to account for the first inelastic scattering event, but also for the rest of the successive inelastic events contributing to the measured spectra. This approach has been shown to be a valid approximation in a previous work [9]. Moreover our model implies a straight line trajectory inside the solid for the photoelectron and thus neglects elastic scattering. However, we have shown in a previous work [38] that elastic scattering effects are of minor importance for the description of low energy losses (i.e. smaller than 30 eV) in photoemission spectra. Elastic scattering can thus reasonably be neglected in this study.

The full XPS spectrum is thus modeled by convoluting the calculated energy loss cross-section, $K_{sc}^{XPS}$ with the primary excitation spectrum, $F(E)$ considered as an input in the calculations. This $F(E)$ spectrum accounts for all effects that are part of the initial photo-excitation process like lifetime broadening, spin–orbit coupling and multiplet splitting. The shape of each peak of $F(E)$ is modeled by a symmetric mixed Gaussian–Lorentzian function [39]:

$$f_{i}(E) = \frac{\exp(-4i\ln 2)M_{i}E_{0}/\beta_{i}^{2}}{1 + 4(1-M_{i}E_{0}/\beta_{i}^{2})^{2}/\beta_{i}^{4}}$$  \hspace{1cm} (5)

where $E_0$, $\beta_i$, and $M_i$ are respectively the peak center, the full width at half maximum and the mixing ratio parameter (which takes the value of 1 for a pure Gaussian function and 0 for a pure Lorentzian function). Eq. (5) was chosen because it has been used for many years by several groups to describe a large variety of spectra and moreover it gives a certain flexibility in the fitting procedure. Thus the total primary spectrum $F(E)$ is the sum of contributions from peaks

$$F(E) = \int_{0}^{\infty} f_{i}(E)dE A_{i}$$  \hspace{1cm} (6)

where $A_i$ is the peak area. This procedure was recently used to determine the Cu 2p primary excitation spectra of Cu, Cu$_2$O and CuO [9].

The cross-sections calculated in Section 4 have been used to simulate the corresponding Ni 2p experimental spectra from NiO and Ni:SiO$_2$, using Eqs. (3)–(6) and adjusting the parameters in $F(E)$ until good agreement with the experiment was obtained. We note that the fitting parameters were determined independently for the two spectra. Fig. 5(a) and (b) shows the experiment and the corresponding $F(E)$ simulation together with the corresponding primary excitation spectrum $F(E)$. The first and second inelastic scattering contributions to the spectrum are also shown. The $F(E)$ spectra (solid lines) correspond to the contributions described in Eqs. (5) and (6) obtained with the parameters listed in Tables 2 and 3 for the NiO and Ni:SiO$_2$ cases, respectively.

We have chosen as kinetic energy reference the position of the most intense peak (i.e. largest area) in the spectra. Peak 2 at 629.05 eV for NiO and peak 1 at 629.30 eV for Ni:SiO$_2$. For the other contributions to the $F(E)$ spectra in Tables 2 and 3, we give the energy difference with respect to this peak (by convention a negative number is for a peak with a larger kinetic energy than the reference peak) as well as the corresponding kinetic energy. By normalization, we have chosen an area equal to one for the reference peak. We have chosen for all peaks a Gaussian–Lorentzian mixing ratio parameter $M_i = 0.5$. The interpretation and labeling of the peaks in Tables 2 and 3 are explained and discussed in Section 6.

Note that in Fig. 5(a) and (b) the actual fitting is done only in the energy range 615–640 eV corresponding to Ni 2p$_{3/2}$ (peaks 1–5 in Tables 2 and 3). In spite of the fact that the fitting was done in this restricted energy range, a good agreement between the theoretical spectrum and the experiment in the full 570–640 eV energy range is observed. Actually, several constrains were imposed in the fitting of the measured $J(E)$ Ni 2p spectra. The Ni 2p$_{3/2}$ contribution to the total Ni 2p emission was considered as a replica of the Ni 2p$_{3/2}$, displaced by 17.50 eV and with half the amplitude. Indeed, this value of 17.50 eV, valid for both NiO and Ni:SiO$_2$, corresponds to the energy difference between the two spin–orbit contributions 2p$_{3/2}$ and 2p$_{1/2}$ [40]. Then, the factor 1/2 between the relative intensities of the doublet peaks comes from the ratio of their respective spin–orbit degeneracies (2j + 1). For p subshells, this factor is equal to 1/2 [39]. This behavior was already observed for Cu 2p emission [9]. On the other hand we let the width of the Ni 2p$_{1/2}$ peaks vary to improve the fit with experiment.
to the total spectrum (and thus the total background) are larger at its maximum and less wide than the corresponding contributions for NiO. This is clearly due to the difference in shape of the corresponding $K_{\text{XPS}}$ for the two materials [see Fig. 4].

At this point it is worth noting that until now we have considered the total XPS spectrum as the multiple convolution of the primary excitation function $F(E)$ with the energy-differential inelastic electron scattering cross-section. However as shown in Ref. [41] it is also possible to obtain $F(E)$ directly by deconvoluting the total spectrum with the same inelastic cross-section. This is done with the formula

$$F(E) = F(E) - \int_{-\infty}^{\infty} K_{\text{XPS}}(E, E') F(E') \, dE'$$  \hspace{1cm} (7)

valid for homogeneous media [42,43] which is implemented in the QUASES software package [44]. It was shown in Ref. [41] that $F(E)$ spectra obtained by the two methods agree. For the present study, using QUASES (i.e. Eq. (7)) with $K_{\text{XPS}}$ for NiO and Ni$_2$SiO$_2$, we basically obtain the same result as above regarding the evaluation of $F(E)$. Fig. 6(a) and (b) shows the QUASES analysis of Ni$_2$p spectra from NiO and Ni$_2$SiO$_2$ samples, respectively, using the corresponding $K_{\text{XPS}}$ cross-sections. The small difference between the two is mainly due to the constraint in fitting the spectra with Eqs. (5) and (6). A fitting of the $F(E)$ obtained with Eq. (7) will result in essentially the same peaks as in Tables 2 and 3. This appears to be a faster and more convenient procedure because the fitting is done directly on the $F(E)$ spectra rather than on the experimental data including the multiple inelastic background which must therefore be calculated for each iteration step in the fitting procedure.

### 6. Discussion

The interpretation of the fine structure of Ni 2p photoemission in nickel oxides has been the subject of a strong debate for more than two decades [10–16]. The ground state is a mixture of $c3d^8$, $c3d^9L$, and $c3d^{10}L^2$ configurations, where $c$ indicates a hole in the Ni 2p core level (either at the $2p_{z}$ or $2p_{x,y}$) and $L$ denotes a hole at the ligand (oxygen) site. This electronic structure gives rise to Ni 2p photoemitted spectra with multiple peaks, which have been widely studied in the past [10–16]. However, most interpretations have been done only at a qualitative level and have been restricted to the Ni 2p$_{z}$ photoemission line. Note that the multiplet splitting of the Ni 2p$_{z}$ photoemission does not need to be necessarily equal to that of Ni 2p$_{x,y}$ due to a difference in interaction with the core hole left behind after the photoemission process. However, we keep this as identical in the fitting procedure and we will discuss the observed differences after the analysis. Fig. 7 shows separately various peaks of the Ni 2p transition for NiO and Ni$_2$SiO$_2$.

The main difference between the two spectra is obviously the absence of peaks 2 and 7 (see Tables 2 and 3 for references of the peaks), but other differences are also observed. The peaks 1 and 6 are displaced by 1.6 eV which is in agreement with previous results (for peak 1) in Refs. [11,19]. Moreover, the intensity of all peaks is different...
for the two samples but their energy position is almost identical (with a maximum difference of 0.15 eV).

In the case of the NiO sample, the Ni 2p3/2 photoemission depicts the typical shape of Ni cations located in an oxygen octahedral coordination (see Ref. [12] for instance). The spectrum is characterized by a main double structure at 629–631 eV kinetic energy (~855–857 eV binding energy) as shown in Fig. 5(a) corresponding to a \( c^3d^9L \) final state and a broad strong shake up structure at ~5–8 eV higher binding energy (lower kinetic energy) corresponding to a \( c^3d^{10}L_2 \) final state (in the following we consider \( c^3d^{10}L_2 \) as the sum of the two contributions \( c^3d^{10}L_2-a \) and \( c^3d^{10}L_2-b \), see Tables 2 and 3). Besides, another minor feature at about 11 eV higher binding energy is observed, which is due to a \( c^3d^8 \) configuration [15]. The \( c^3d^8 \) state is split into two bands (\( c^3d^8L/c^3d^8L-nl \)), where the latter is mainly due to non-local ("nl") screening effects [14,16]. The band at higher binding energy is usually considered as due to a non-local screening process from the oxygen electron cloud belonging to the outer NiO6 clusters. The relative intensity of these two contributions is extremely sensitive to sample preparation [12].

Because the present analysis is quantitative, we are able to report relative intensities of the different states that contribute to the Ni 2p photoemission, together with the corresponding widths. Thus, the relative intensity ratio of the \( c^3d^8L/c^3d^{10}L_2/c^3d^8 \) configurations is 1.40/1.16/0.17 for the case of NiO samples (or equivalently 1.0/0.83/0.12). Note that this quantitative evaluation was not possible in previous works because the standard Shirley background was usually applied to isolate these peaks (and in some case no background was subtracted).

Another significant result is the relative intensity ratio between the two contributions to the \( c^3d^8L \) configuration. It is found that the \( c^3d^8L-nl/c^3d^8L \) intensity ratio is 2.5. This large value might be related to the amorphous structure of the sample. For single crystalline NiO(100) an estimated value of ~1 has been reported [10] but without a proper quantitative analysis. It is also worth noting that this non-local splitting is present also in the Ni 2p1/2 photoemission peaks but it is not resolved because the peak is wider due to the shorter lifetime of this process.

At this point we note that the multiplet splitting found by fitting the Ni 2p1/2 emission also reproduces rather well the Ni 2p3/2 photoemission. We keep the same multiplet peak structure letting only the width of the peaks vary to improve the fit to the experiment (see Table 2). The fit in the Ni 2p1/2 region is excellent, except at the high binding energy side (804 eV kinetic energy) where there is some intensity mismatch. This indicates that the account of the \( c^3d^8 \) final state to

Fig. 6. QUASES analysis of Ni2p photoemission spectra from (a) NiO and (b) Ni:SiO2: experimental spectrum (dashed line), background (dotted line) and F(E) spectrum (solid line). Also shown (dash-dot) is the F(E) obtained from the fitting procedure using Eqs. (3)–(6).

Fig. 7. Various peaks contributing to the total F(E) function for (a) NiO and (b) Ni:SiO2. Peaks are referenced as it is done in Tables 2 and 3: 1 and 6: \( c^3d^9L \); 2 and 7: \( c^3d^9L-nl \); 3 and 8: \( c^3d^{10}L_2-a \); 4 and 9: \( c^3d^{10}L_2-b \); and 5 and 10: \( c^3d^8 \) (the peaks 1–5 correspond to Ni 2p3/2 emission and peaks 6–10 to Ni 2p1/2 emission).
the Ni 2p1/2 photoemission is not just a replica of what is seen in the Ni 2p3/2 multiplet. As we will see later this mismatch intensity is also present in the analysis of the Ni 2p emission of the Ni:SiO2 sample. Thus, this might also be an indication of a small deviation of the theoretical Ni 2p3/2/Ni 2p1/2 branching ratio.

For Ni:SiO2, Ni is a minority species in a SiO2 matrix and the non-local peak disappears (see Table 3). The peak at 629.05 eV kinetic energy vanishes and only the peak at 630.90 eV kinetic energy remains but displaced to 629.30 eV kinetic energy (with an increased intensity), indicating a strong distortion of the local octahedral structure characteristic of NiO due to the presence of Si as second neighbor to Ni. Note that due to the low concentration of Ni within the SiO2 matrix (about 5%) and to the fact that the Ni atoms are randomly dispersed within the film, the local coordination of the Ni2+ ions will most probably be tetrahedral, forced by the silica network. As expected, the corresponding counterpart of the 629.05 eV peak for the 2p1/2 contribution (peak 7 in Table 3) also disappears.

The relative intensity ratio of the c3d5/2Lc3d10L2/c3d8 configurations is 1.0/0.83/0.11 for the Ni:SiO2 samples for both the Ni 2p3/2 and Ni 2p1/2 peaks. Thus, while the intensity of all peaks is considerably different between the two samples, it is noteworthy that the relative intensity ratio is equal for NiO and Ni:SiO2. It is possible to deduce this because we use an accurate quantitative model to evaluate the background.

7. Conclusion

In this paper we determine the primary excited spectra of Ni 2p photoelectron emissions of NiO and Ni:SiO2 samples prepared by reactive magnetron sputtering at room temperature. It relies on a quantitative dielectric description of the photoemission process and the electron transport. It is found that the intensity ratio between the Ni 2p c3d5/2/c3d10L2/c3d8 final states is equal for NiO and Ni:SiO2 samples and follows the 1.0/0.83/0.11 intensity ratio. It is also found that the simple description of the 2p1/2 emission as a spin–orbit shift replica of the 2p3/2 emission accounts reasonably well (but not exactly) for the corresponding measured signal. Finally it is also reported that direct evaluation of the primary excited spectra F(E) can be found by standard QUASES peak shape analysis using the inelastic scattering cross-sections K\text{XPS} obtained from the dielectric description of the electron energy losses described in Refs. [3,4].

Acknowledgments

The research leading to these results has received funding from MINECO (Spain), grant no. MAT2013–40852R and from the Danish Council for Independent Research (Natural Sciences).

References