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Study of the growth of NiO on highly oriented pyrolytic graphite by X-ray absorption spectroscopy

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Abstract

In this work, we present a X-ray absorption spectroscopy (XAS) study of the growth of NiO on highly oriented pyrolytic graphite (HOPG). NiO has been grown by reactive evaporation of metallic Ni in an oxygen atmosphere (2×10^{-5} Torr) at room temperature. We paid special attention to the study of the early stages of growth. Both, Ni 2p and O 1s core-level XAS spectra were measured. For large NiO coverages, the spectra resemble that of a NiO single crystal, thus indicating the formation of a stoichiometric NiO thin film on the HOPG substrate. The Ni 2p XAS spectra remain similar during the whole growth process, indicating that Ni atoms are present in the high spin Ni^{2+} form, as supported by multiplet calculations. In contrast, for low coverages the line-shape of the O 1s XAS spectra differ strongly from that of bulk NiO. Cluster calculations of the spectra in octahedral and pyramidal symmetries support the formation of nanometric planar NiO islands at the graphite steps as previously observed by atomic force microscopy (AFM) in this system.

Keywords: Nickel oxide; NiO nanostructures; X-ray absorption spectroscopy

1. Introduction

The main purpose of this paper is the study of the electronic structure of the early and final stages of growth of a NiO thin film on highly oriented pyrolytic graphite (HOPG). This work is motivated by the increasing importance of nanostructured oxide coatings in technological applications. In fact, NiO is an oxide material with applications in catalysis and as magnetic materials. Another important motivation is that a previous atomic force microscopy (AFM) study on this system shows that for the early stages of growth, NiO grows by forming planar islands (100–200 nm in size and 3–10 nm in height), mainly located at the HOPG steps. For further NiO deposition, the NiO islands spread throughout the terraces, reaching coalescence for higher NiO coverages [1]. Therefore, the study of the electronic structure of this nanostructured system seems to be well justified. We show below that the X-ray absorption spectroscopy (XAS) spectra reflect surface effects due to the large surface to volume ratio typical of nanometric structures.

X-ray absorption spectroscopy is a well established technique which, in a first approximation, probes unoccupied electronic states. However, the Ni 2p XAS spectra are dominated by the Ni 2p spin-orbit splitting, as well as the Ni 2p–3d Coulomb and exchange interactions. These interactions give rise to strong multiplet effects in the resulting spectra, hiding the information on the density of states [2]. These effects are, in turn, very sensitive to the local symmetry of the initial state, thus being a suitable technique to determine the chemical state of the metal [3].

The O 1s XAS spectra correspond to O s $\rightarrow$ p transitions where, according to the dipole selection rule ($\Delta\ell = \pm 1$) in XAS, only unoccupied O states of p-character can be reached. The spectra are thus, directly related to unoccupied O p states mixed with metal-3d and metal-4sp states via hybridization. The near-edge region of the spectra is dominated by hybridization with metal-3d states, thus mapping the metallic 3d density of states. This property of XAS allowed us to observe the splitting of the Ni 3d states located at the NiO surface in nanostructured NiO systems [4]. It is worthy to note here that NiO is a $3d^8$ charge transfer oxide with the ground state as a mixture of $3d^8 + 3d^9\underline{L} + 3d^{10}\underline{L}^2$ states [5–7] so that only e_g states remain unoccupied. We show below that surface effects are clearly observed in the O

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1s XAS spectra of the nanostructured NiO system studied here which are completely consistent with the AFM data.

2. Experimental

The experiment was performed in an ultra high vacuum chamber located at the PM4 beam-line in the Synchrotron BESSY (Berlin). Successive depositions were performed and analyzed by XAS. NiO was deposited at room temperature on HOPG by reactive evaporation from a pure Ni filament. The evaporation was performed in an oxygen atmosphere (5×10^{-5} Torr) at room temperature. The evaporation rate was constant and maintained low enough to allow the study of the early stages of NiO growth. After deposition for large coverages, the sample was annealed at 400 °C for 30 min in ultra high vacuum. More details on the preparation procedure can be found elsewhere [4].

The XAS measurements were performed at the PM4 beamline of the BESSY II storage ring (Berlin). The spectra were collected in the total electron yield detection mode at grazing incidence to take advantage of the linear polarization of the synchrotron light in order to enhance transitions towards atoms in the direction to the surface normal (surface enhancement). The estimated overall resolution of the plane grating monochromator (PM4) was better than 100 meV at the O 1s edge (530 eV). The spectra were normalized to the I_0 current coming from a fresh gold sample in order to correct the spectra from the contamination of the optical elements and beam losses.

3. Results and discussion

The Ni 2p XAS spectra as a function of the NiO coverage are shown in Fig. 1. We have to note here that the coverages have been calculated from the intensities of the XAS spectra following conventional methods and assuming a layer-by-layer way of growth at constant evaporation rate. Since the AFM data show that the way of growth of NiO/HOPG is dominated by the formation of nanometric planar islands, the coverage should be understood as an indication of the equivalent material needed to complete such layers. At first sight, all the spectra through the series are similar. First of all we want to note that the spectrum of the NiO thin film annealed at 400 °C matches other published Ni 2p spectra for bulk NiO [8,9]. Also, the spectra for large coverages, prior to annealing, are almost identical. This is a clear indication that a stoichiometric NiO thin film can be grown on the HOPG substrate. However, the most important feature is that the Ni 2p XAS spectra show the same line-shape during the whole growth process. Even for low coverages, the structures observed in the spectra are the same, although less defined and slightly broader, than those for bulk NiO. These minor discrepancies can be attributed to disorder and consequently to a lower value of the crystal field. The spectra also slightly shift towards higher photon energies as the coverage increases. Although XAS measurements cannot be referred to the Fermi level, this shift is directly related to the increase of the thickness of the NiO isolating thin film. These results seem to indicate that the oxidation

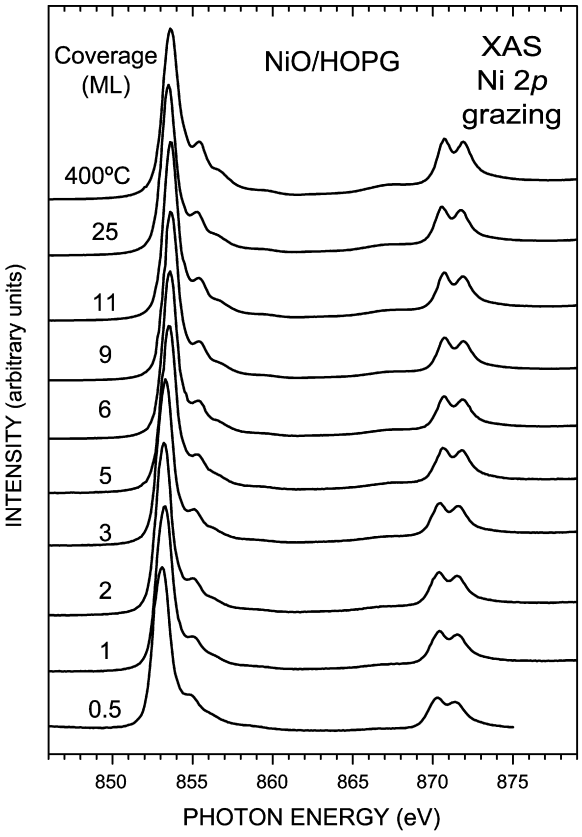

Fig. 1. Ni 2p XAS spectra as a function of the NiO coverage.

state of the Ni atoms remains unchanged and the same as in bulk NiO.

In order to corroborate the above results, we have compared the Ni 2p XAS spectra with theory. According to de Groot et al. [2,3], the spectra can be reproduced by calculating the 2p → 3d multiplet transitions as a first step. In the case of NiO, these transitions have to be projected in an octahedral crystal field of certain strength. We have performed 2p → 3d multiplet calculation for Ni ions in different symmetries: high spin Ni^{2+} (Fig. 2a), low spin Ni $^{2+}$ (Fig. 2b) and Ni^{3+} (Fig. 2c). The crystal field parameter ($10Dq$) was set to 1.8 eV in all calculations. From the comparison of the calculations with the experimental Ni 2p spectra it is inferred that, indeed, the Ni atoms involved in the experiment remain in the high spin Ni^{2+} form.

Fig. 3 shows the O 1s XAS spectra as a function of the coverage. Once again, the spectrum of the annealed thin film is identical to other spectra published elsewhere for bulk NiO [10,11]. The first peak at 530.5 eV is assigned to the hybridization of O p states with Ni 3d (e_g) states whereas the broad peaks located at 536.0 and 539.0 eV correspond to O p states hybridized with Ni 4s and Ni 4p, respectively. The spectra for high coverages prior to annealing are also similar to that of bulk NiO. This supports again the growth of a stoichiometric NiO thin film on the HOPG substrate.

However, for low coverages (0.5 ML in Fig. 3) the spectrum differs strongly from the bulk spectrum. The single peak at threshold, assigned to e_g states in bulk NiO, is now split forming a broad band. It is clearly seen that the initial broad band for the

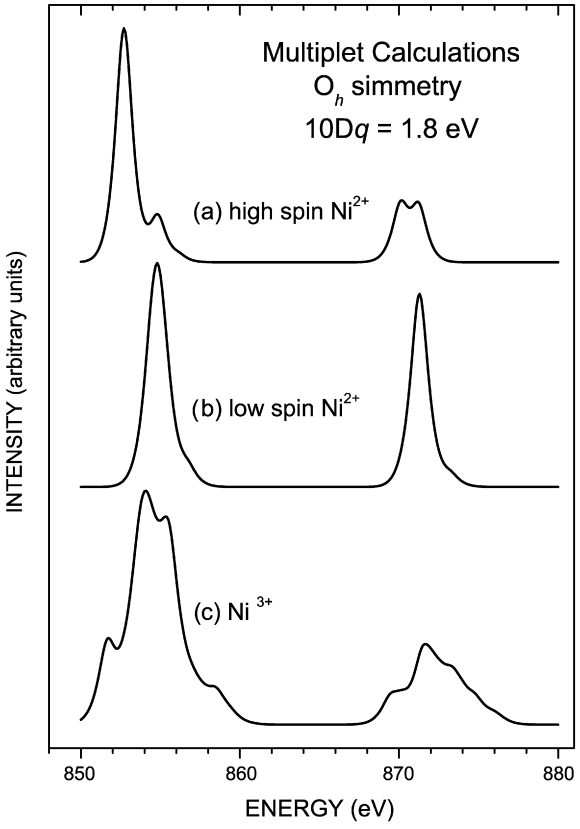

Fig. 2. Multiplet calculations for: (a) Ni^{2+} with high spin symmetry; (b) low spin Ni^{2+}; (c) Ni^{3+}.

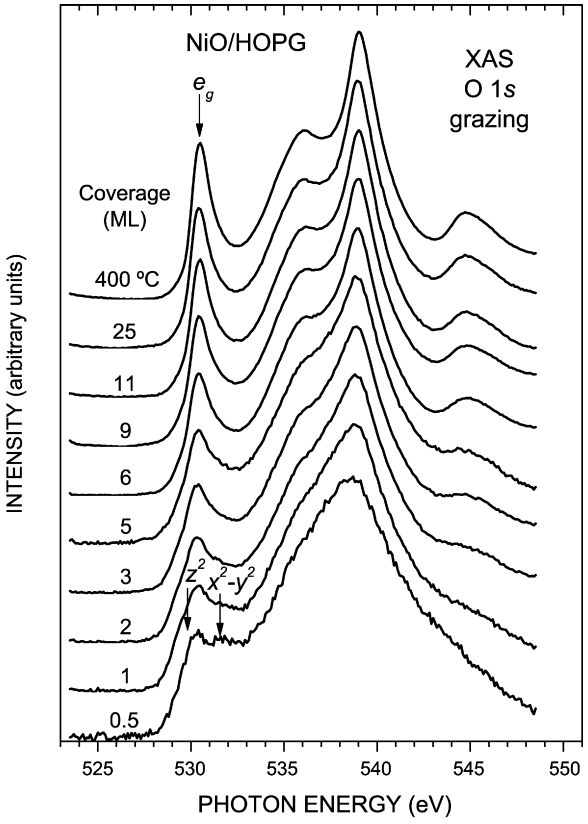

Fig. 3. O 1s XAS spectra as a function of the NiO coverage.

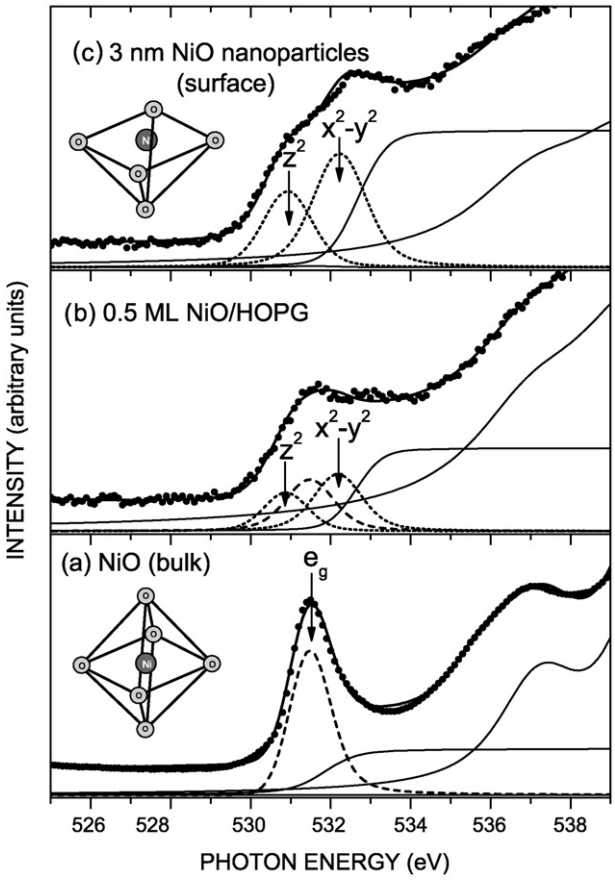

Fig. 4. Experimental and calculated near edge region of the O 1s XAS spectra (dots) of: (a) large NiO coverage (bulk); (b) 0.5 ML NiO/HOPG; (c) 3 nm NiO nanoparticles. Gaussian curves represent the results of the calculations in: octahedral (short dash lines) and pyramidal symmetry (short dot lines). Solid lines represent typical curves used to fit the background.

very low stages of growth is progressively changing in shape throughout the series to give the final bulk line-shape.

To understand this effect we have calculated the O 1s absorption edge by means of cluster calculations in octahedral (NiO_6) and pyramidal (NiO_5) symmetries. The results of the calculations are presented in Fig. 4. The calculations in octahedral symmetry (short dash line in Fig. 4a) give a single peak which corresponds to the hybridization with the unoccupied e_g states in bulk NiO, as it is seen by the comparison with the experimental O 1s XAS spectra of bulk NiO (dots in Fig. 4a). In turn, the calculations for pyramidal symmetry (short dot line in Fig. 4c) give two peaks separated by 1.5 eV and with relative intensity of 32% and 50% with respect to the intensity of the bulk line.

These results show that unoccupied e_g states split into z^2 and $x^2 - y^2$ states due to the lack of the apical oxygen at the NiO surface. The calculations in pyramidal symmetry have been compared with the experimental O 1s XAS spectra of 3 nm NiO nanoparticles taken from Ref. [12]. This nanometric system shows important surface effects due to the high surface to volume ratio. The calculations perfectly agree with the spectra of the NiO nanoparticles. However, in the case of the spectra of 0.5 ML of NiO/HOPG, the best fitting has been obtained by introducing

a small component of the bulk calculations. We have to note here that all the XAS spectra shown here have been taken at grazing incidence to enhance the surface of the planar NiO islands. The quasi-bidimensional morphology of the NiO islands is reflected in the XAS spectra. The planar islands formed at the early stages of growth present a large surface to volume ratio, allowing the observation of this surface effect. It can be seen that further evaporation produces the increase of the bulk component, indicating an increase of the island thickness. Only when coalescence has been reached (25 ML in Fig. 3), the thin film spectra resemble those of bulk NiO. Another relevant aspect of the results is the presence of a z^2 dangling bond that can be related to the well known catalytic properties of NiO nanoparticles. In this way, the early stages of growth of NiO on HOPG seem to be a suitable system to prepare NiO catalysts.

4. Conclusions

We have studied the electronic structure of the growth of NiO thin films on graphite substrate by means of XAS. In general, the spectra reflect the nanostructured morphology of the early states of growth, in agreement with previous AFM studies. Whereas the Ni 2p XAS spectra indicate that Ni species are always in the high spin Ni^{2+} form, the O 1s XAS spectra show that for the early stages of growth a splitting of the Ni z^2 and $x^2 - y^2$ of the Ni atoms located at the surface of the islands is produced. This is consistent with the structural morphology of the planar nano-islands observed with AFM. More studies on the catalytic properties of the early stages of growth of NiO on HOPG are suggested.

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