Splitting of the Ni 3d states at the surface of NiO/HOPG nanostructures

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This project deals with the study of the electronic structure of the NiO nanostructures formed at the early stages of growth of NiO on highly oriented pyrolytic graphite (HOPG). Our main aim is the study of nanostructured NiO systems where possible surface effects are enhanced by the large surface to volume ratio of the nanostructures. In fact, early studies [1] on 3 nm NiO nanoparticles with unique catalytic properties revealed a splitting of the unoccupied Ni e_g states, as shown by the O 1s XAS spectra. This splitting was interpreted as the result of the lack of the apical oxygen at the NiO surface and the large surface to volume ratio of the nanoparticles. On the other hand, the early stages of growth of NiO/HOPG are known to produce planar NiO islands along the graphite steps as shown by Atomic Force Microscopy (AFM) images.[2] Such a particular arrangement of NiO nanostructures is expected to exhibit similar surface effects as in the NiO nanoparticles. Therefore, the study of this system seems to be well justified.

NiO was deposited on HOPG by reactive evaporation from a pure Ni filament in the preparation chamber. The HOPG substrate was cleaved in air just before being introduced in the preparation chamber. Then, it was thermally annealed in UHV at 300^{o}C to remove any possible surface contamination. Reactive evaporation was performed in an oxygen atmosphere (5×10^{-5} Torr), with the substrate kept at room temperature. The oxygen gas was aimed directly to the sample using a narrow pipe to enhance the oxidation efficiency. The evaporation rate was maintained low enough to study the early stages of NiO growth in more detail. After each XAS analysis, the substrate was introduced in the preparation chamber for the successive evaporations.

XAS measurements were performed at the PM4 plane grating monochromator in the BESSY II storage ring (Berlin). This experiment requires a high photon flux in order to detect an acceptable signal from the small amount of NiO. The optical arrangement of this monochromator was set to optimize both, high photon flux and resolution. The estimated overall resolution was better than 100 meV at 530 eV. The spectra were collected in the total electron yield detection mode. In order to observe possible dichroism effects, the spectra were measured at normal and grazing angles with respect to the incident light. The spectra were normalized to the I_0 current, measured from a clean gold sample, to correct for the beam current. The NiO coverage was calculated from the O 1s XAS intensities following conventional methods. Since the growth of NiO on HOPG is not in a layer-by-layer mode, the estimated coverages should be understood as the equivalent material to form a monolayer.

Fig. 1 shows the O 1s XAS spectra of the NiO overlayers for (a) low and (b) large coverages. For large coverages, the spectrum is in very good agreement with previous spectra published for bulk NiO. This shows that a thin film of stoichiometric NiO can be grown on HOPG at room temperature using this growth method. The unoccupied density of electronic

states (UDOS) of O *p* character obtained by *ab-initio* band- structure calculations for antiferromagnetic NiO, are also shown in Fig. 1(c). The spectrum for low coverages (0.5 ML) presents significant differences with respect to that of large coverages, i.e., bulk NiO. The most relevant change in the spectra concerns the e_g region, which is shown in more detail in the inset of Fig. 1. The well defined e_g peak in bulk NiO is split in two broad and unresolved peaks for 0.5 ML of NiO/HOPG. The Ni 3d states in NiO are split by the octahedral crystal field produced by the O into the t_{2g} and e_g sub-bands. However, the lack of the apical O at the surface of NiO breaks the symmetry and results in a pyramidal crystal field. This effect produces the additional splitting of the e_g sub-bands observed for low coverages, where the relative weight of the surface states is much larger than for bulk NiO.

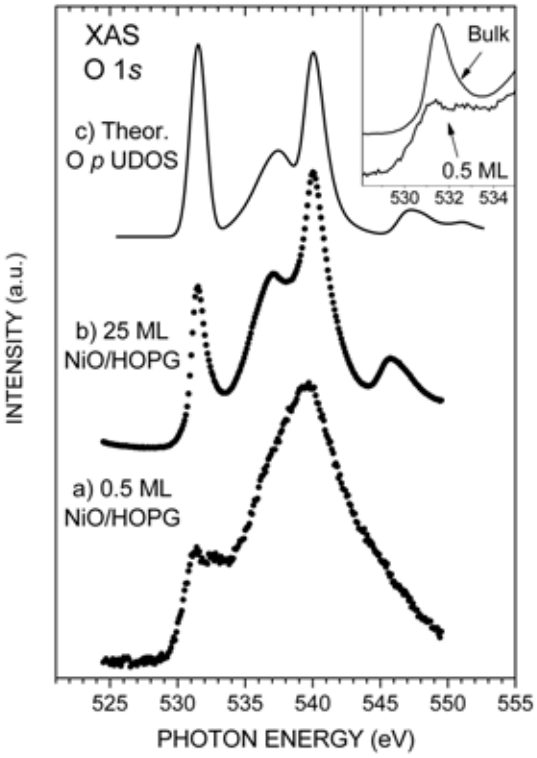

Fig. 1: O 1s XAS spectra for low (a) and large (b) coverages of NiO on HOPG

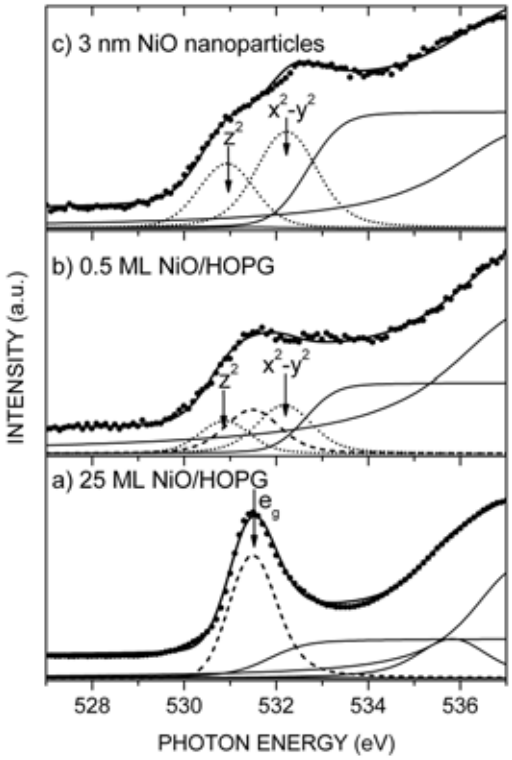

Fig. 2: Near edge region of the O 1s XAS spectra for (a) low, (b) large coverages of NiO on HOPG and 3 nm NiO anoparticles.

To corroborate this theory, we have calculated the O 1s XAS spectra using cluster model calculations in octahedral and pyramidal symmetries. Fig. 2 shows the near-edge region of the experimental spectra of: (a) large and (b) low coverages of NiO/HOPG. The spectra have been fitted using Lorentzian curves at the positions given by the calculations together with other typical functions in the fittings of XAS spectra to simulate the background and the tails of the higher energy structures. The octahedral calculation for bulk NiO shows a single line (short dash) corresponding to transitions to e_g states. The pyramidal calculation for surface NiO presents two lines (short dots) corresponding to the x^2-y^2 and z^2 final states. As shown in Fig 3(a) the agreement with the spectrum of bulk NiO is excellent. To fit the spectrum of the NiO sub-monolayer, shown in Fig. 2(b), not only the two surface components have been used but also a small contribution of the bulk component has been included.

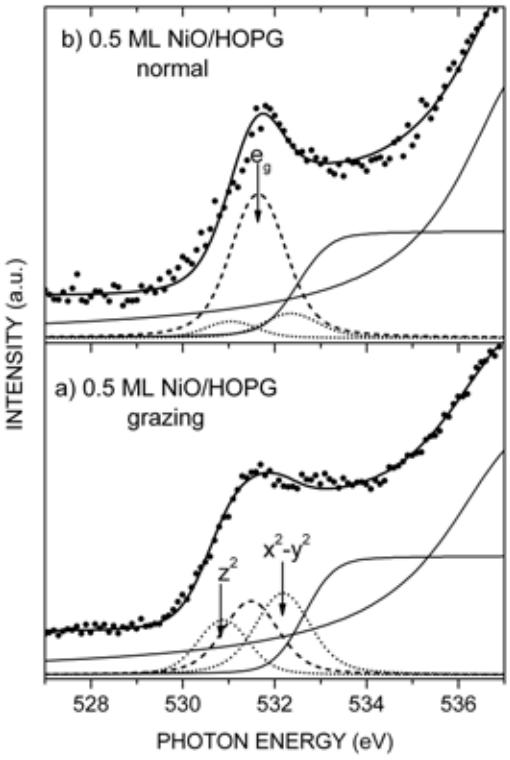

Fig. 3: Near edge region of the O 1s XAS spectra of 0.5 Ml of NiO/HOPG taken at: a) grazing and b) normal incidentes.

Fig. 2(c) shows the near edge region of the O 1s XAS spectrum of 3 nm NiO nanoparticles fitted with the surface components. The excellent agreement with the calculations confirm the interpretation of the O 1s XAS spectrum of NiO nanoparticles made in Ref. 1, and strongly suggests that the same splitting mechanism is operating in the case of (0.5 ML) NiO/HOPG.

Fig. 3 shows the O 1s XAS spectra of 0.5 ML NiO/HOPG taken at (a) grazing and (b) normal photon incidence. The spectra exhibit a clear dependence (dichroism) with the relative polarization of the incident light. The normal incidence spectrum, with the electric field **E** parallel to the surface, resembles that of bulk NiO with a relatively broader single e_g peak (short dash). In particular, the distinct splitting due to surface effects (short dots) is very week in this spectrum. On the other hand, in the grazing incidence spectrum, with the electric field **E** perpendicular to the surface, the double peak (x^2-y^2 and z^2) structure (short dots) is clearly observed. The dichroism effect shows that the splitting affects mostly the states perpendicular to the surface, and supports the idea that the splitting is related to the absence of the apical oxygen at the surface. It is worth noting that, in this case, the z^2 orbital forms a dangling bond perpendicular to the surface. This might be related to the enhanced catalytic activity of the larger surface/bulk ratio NiO nanostructures.

In summary, in this work, we have studied the electronic structure of the NiO nanostructures formed at the early stages of growth (0.5 ML) of NiO on HOPG. The results have been compared to those of and 3 nm NiO nano-particles. The Ni 2p XAS spectra of the NiO planar islands confirm that Ni atoms are present in the high spin Ni^{2+} form. On the other hand, the O 1s XAS spectra show exactly, as in the NiO nanoparticles, a splitting of the e_g band which is explained as due to the lack of the apical O atoms at the surface.

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