

Ni 3d surface states in NiO nanostructures

L. Soriano¹, A. Gutiérrez,¹ M. Abbate,² I. Preda,¹ S. Palacín¹

¹Departamento de Física Aplicada C-XII, Universidad Autónoma de Madrid, Cantoblanco
E-28049 Madrid, Spain

²Departamento de Física, Universidade Federal do Paraná, Caixa Postal 19091, 81531-990
Curitiba PR, Brazil

l.soriano@uam.es

This abstract 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. Reactive evaporation was performed in an oxygen atmosphere (5×10^{-5} Torr), with the substrate kept at room temperature. 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). 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. 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 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.

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.

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 Ni²⁺ 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.

References:

- [1] L.Soriano, M.Abbate, J. Vogel, J.C. Fuggle, A. Fernández, A.R. González-Elipe, M. Sacchi and J.M. Sanz, Chem. Phys. Lett. **208**, (1993) 460.
 [2] C. Morant, L. Soriano, J.F. Trigo and J.M. Sanz, Thin Solid Films, **317**, (1998) 59

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

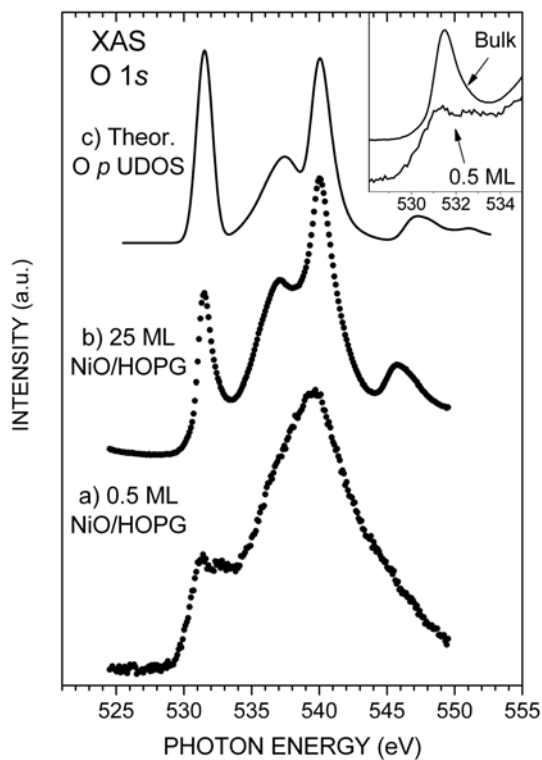


Fig. 2: Near edge region of the O 1s XAS spectra for (a) low, (b) large coverages of NiO on HOPG and 3 nm NiO nanoparticles.

