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Report:

During this experiment we have performed a structural study of NiO films of thickness T = 3 and 10 monolayer (ML) grown on Ag(001). The interest of such systems lies in the fact that the energy gap (E_g) of the oxide, in the oxide/metal system, can be modulated as a function of T.[1] The demonstrated ability to control T represents therefore a new technological opportunity for band-gap-engineering.

Polarization-dependent X-ray absorption spectroscopy at the Ni K-edge has been performed using three different orientations θ between the NiO growth axis and the electric field (E) of the photon beam: θ = 15°, 45° and 75°. The data analysis, performed in the frame of the multiple scattering approach, allowed us to obtain an accurate description of the local atomic environment of the Ni atoms up to the seventh coordination shell, including the determination of the in-plane and out-of-plane strains for the NiO films (determined with an accuracy better than 1%, resulting from the determination of Ni-O bond distances with a statistic error lower than 0.01 Å). See Figure 1 to appreciate the quality of the fits. Within the experimental errors, the 3ML film has both in and out-of-plane Ni-O distances compatible with those expected in the case of perfect pseudomorphism on Ag(001). A rough film morphology, possibly including also the presence of NiO islands, is also suggested by the optimized coordination numbers. Conversely the 10 ML film is partially relaxed without significant deviation from ideal bidimensional film. The present EXAFS study allows to rule out any significant atomic interdiffusion process between the substrate and the NiO film. Comparison with previous litterature data allows us to hypothesize a two steps growth mechanism for NiO films on Ag(001). The detection of a Ni-Ag contribution in the EXAFS signal of the 3 ML sample collected at θ = 15° allowed us to determine the NiO-Ag(001) interface distance: $d_{\text{interface}} = 2.36 \pm 0.05$ Å. This value is expanded if compared to both NiO and Ag half lattice parameters (2.088 and 2.045 Å respectively).

To validate the picture emerging from EXAFS experimental data, we have also performed periodic *ab initio* calculations with CRYSTAL code.[2] The supported film was simulated by a two-dimensionally periodic slab of five layers of silver atoms parallel to the (001) face, epitaxially covered on both sides with 2 ML of NiO. A hybrid-exchange Hamiltonian was adopted because of its satisfactory performance in describing the bulk properties of both silver and nickel oxide, and a basis set of triple-zeta quality was used for all atoms. The equilibrium geometry of the substrate, and that of an epitaxial NiO monolayer was there determined. In particular, the O-on-top configuration was found more stable than the Ni-on-top one by 0.25 eV/NiO unit. The z coordinates of all atoms of the oxide have been optimised. The energetic and geometric features of the optimised structure are as follows: interaction energy per NiO unit from 0.21 eV; distance between O and Ag surface 2.46 Å; $d_{\text{interface}}$ 2.40 Å; $r_{//}$ has been constrained to 2.07 Å (pseudomorphism model) while $r_{\perp}$, is 2.10

Å. The 2.10 Å value, corresponds to the average between the O_1-Ni_2 (2.07 Å) and Ni_1-O_2 (2.13 Å) distances, where the suffix (1 or 2) reflects the NiO layer from the Ag surface (first or second). $r_{//}$ = 2.10 Å is in excellent agreement with the Ni-K edge EXAFS value: 2.118 ± 0.02 Å. The same holds for $d_{\text{interface}}$ = 2.40 Å, to be compared with $d_{\text{interface}}$ = 2.37 ± 0.05 Å. We do not believe that this theoretical result could be altered by considering thicker overlayers. Figure 2 summarizes the our experimental and theoretical data.

Results from this experiment have been published in three articles.[3-5]

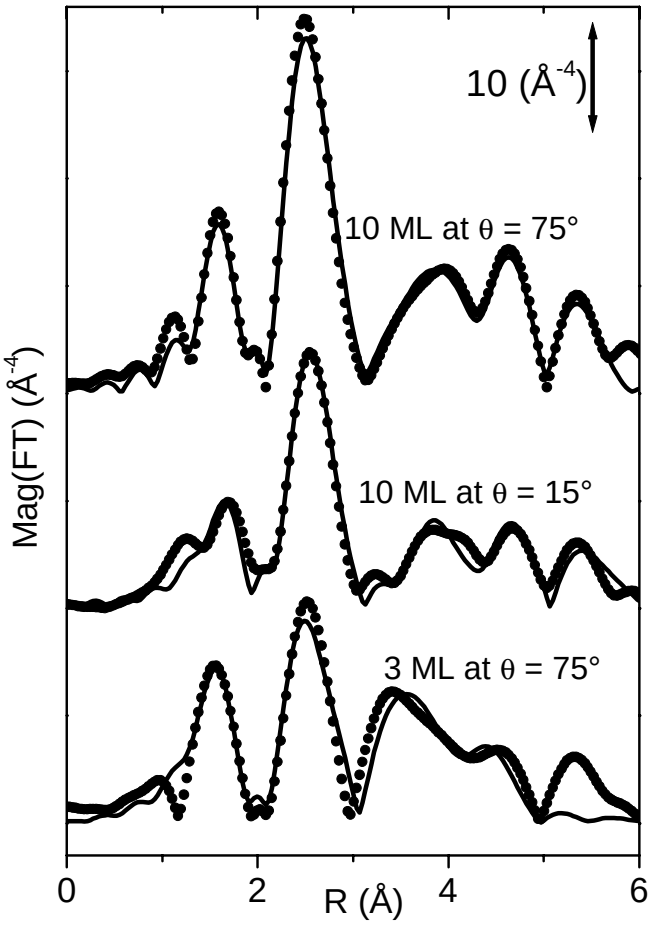

Fig. 1. Comparison between experimental (points) and best fit (solid line) for the modulus of the k^3-weighted, phase uncorrected, FTs of the experimental χ(k) of 10ML(θ=75), 10ML(θ=15) and 3ML(θ=75), vertically shifted for clarity. Only signals from the tetragonally distorted NiO film contribute to the fit, performed in the 1.0-5.8 Å and in the 1.0-5-1 Å R-ranges for the 10 and 3 ML samples respectively.

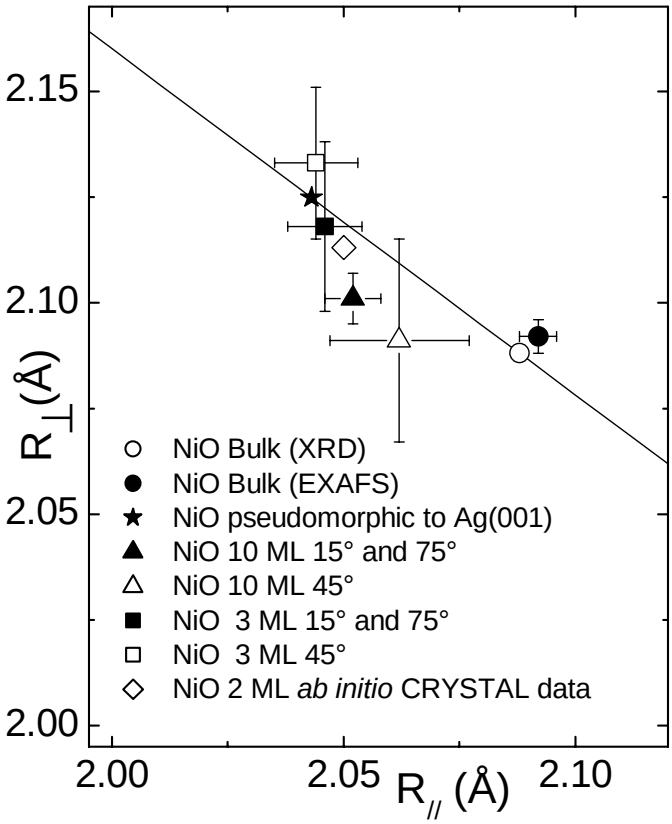

Fig.2 Out-of-plane Ni-O bond distance *vs*. in-plane one of thin NiO films: full square 3ML(θ=15, 75), open square 3ML(θ=45), full triangle 10ML(θ=15, 75), open triangle 10ML(θ=45) and full circle sintered NiO determined in this EXAFS study. Diamond reports the *ab initio* data. Straight line represents the theoretical $R_\perp$ *vs*. $R_{//}$ relationship predicted by the elastic theory, adopting the Poisson ratio of the NiO bulk (γ = 0.818). Big dot is the unstrained NiO bulk (XRD), the star represents the ideal perfect pseudomorphism of NiO on Ag(001).

References

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