

**Experiment title:**

Study of the local coordination of Co atoms at the CoO/oxide interfaces

Experiment number:**25-01- 883****Beamline:****BM 25 A****Date of experiment:**

from: 06 March 2013 till: 10 March 2013

Date of report:**30/05/2013****Shifts:****12****Local contact(s):****E. SALAS***Received at ESRF:***Names and affiliations of applicants (* indicates experimentalists):**

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Report:

The main goal of this project was the study of the local coordination of Co atoms at the CoO/oxide interfaces. To this end, we have measured two sets of samples, containing 3 and 20 equivalent monolayers (ML's) of CoO on selected oxides substrates. We have used SiO₂ (strongly covalent), MgO (strongly ionic) and Al₂O₃ (intermediate) single crystals as substrates. The samples were grown by reactive thermal evaporation of metallic Cobalt in an oxygen atmosphere ($2 \cdot 10^{-5}$ mbar). The samples were analyzed *in situ* by XPS, showing the characteristic Co 2p XPS spectra of CoO (Co²⁺). Co K-edge XANES and EXAFS spectra were measured, *ex-situ*, at the SpLine BM-25A beamline at the ESRF. Measurements were carried out at room temperature in fluorescence mode, using a multi-element solid-state multichannel detector. The low signal to noise ratio prevented us of performing a detailed quantitative EXAFS analysis. However, the XANES spectra gave us important information about the effect of the substrates on the deposited CoO layer.

The Co K-edge XANES spectra corresponding to the samples of 20 Eq-ML's of CoO grown on the substrates (as labelled) are shown in Figure 1. At a first glance, all the spectra are rather similar, showing the same structures at the same energies. Besides, the spectra match that for bulk CoO as reported in the literature [1]. According to the above results we can confirm the formation of a 20 Eq-ML's thin film of CoO on all the substrates. Besides, this layer is stable during its exposure to atmosphere in the meantime from the XPS and XANES measurements.

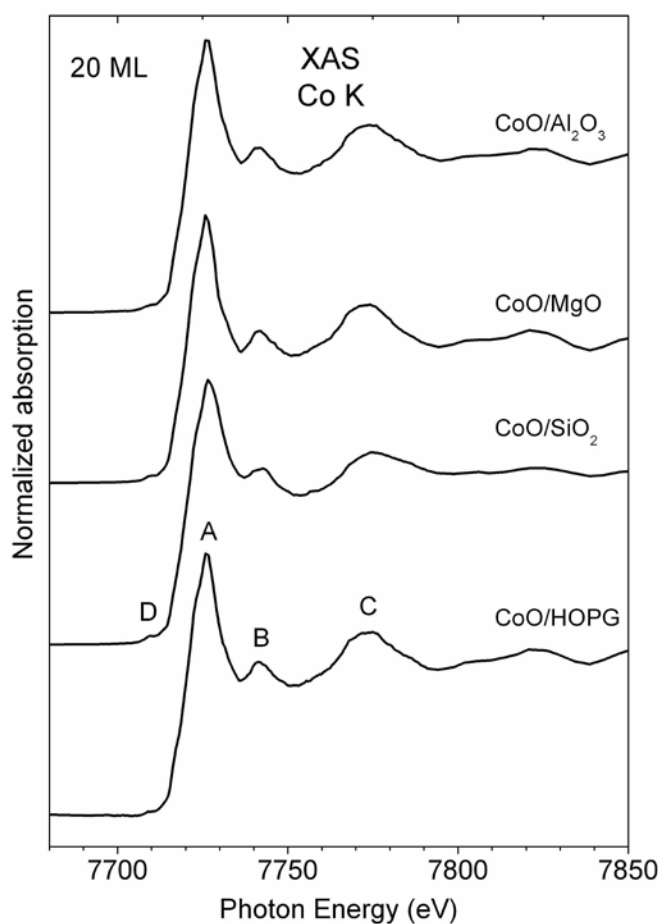


Figure 1: Co K NEXAFS spectra of 20 Eq-ML of CoO grown on the substrates.

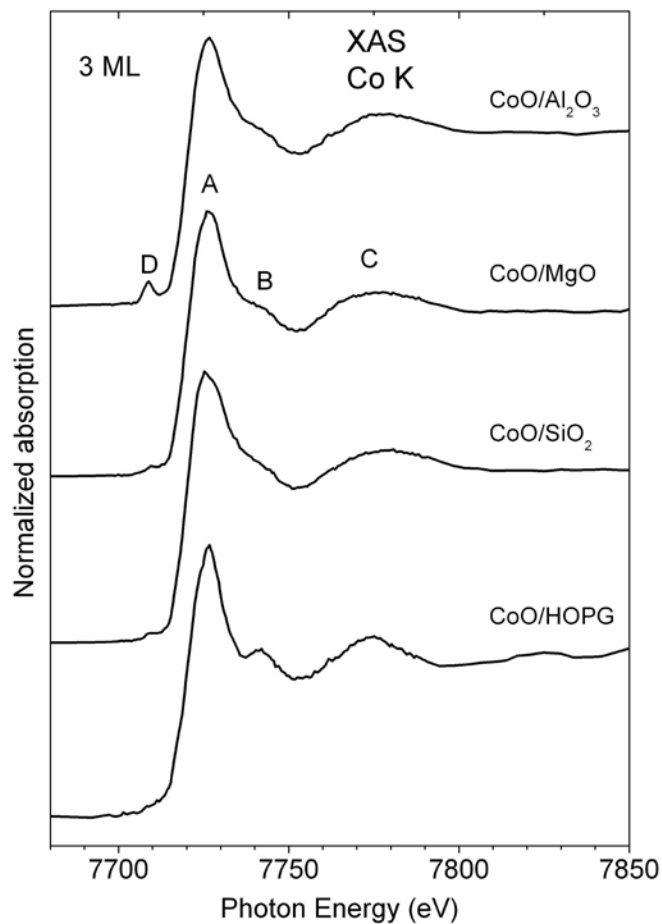


Figure 2: CoK NEXAFS spectra of 3 Eq-ML of CoO grown on the substrates.

On the other hand, figure 2 shows the Co K-edge XANES spectra corresponding to 3 Eq-ML of CoO grown on the same substrates. In this case, the spectra of the CoO ML's grown on the selected oxides do not match those corresponding to large coverages, with the exception of samples grown on HOPG for which the spectra obtained for low- and high-coverages on the same substrate are similar. Two important differences between the spectra for high and low coverages on the oxide substrates have to be pointed out. Firstly, the well defined structure at 7740 eV (labeled as B) appearing in the spectra for large coverages, is smeared out in the spectra for low coverages. Secondly, the weak prepeak appearing at 7710 eV in the spectra for large coverages (labeled as D), is significantly increased in the spectra for low coverages, specially in the spectra of CoO grown on Al_2O_3 . The effect of the smearing out of the peak at 7740 eV can be regarded as the local order around Co atoms is limited to the first two coordination shells [2]. The increase of the intensity of the prepeak located at 7710 eV can be accounted for in terms of the distortion of the octahedral coordination of the Co atoms [3]. This effect is much more intense in the case of the Al_2O_3 substrate where the prepeak is clearly higher than for the rest of the substrates. Recently, Density Functional Theory (DFT) calculations indicate that the most stable phase at the $\text{CoO}/\text{Al}_2\text{O}_3$ interface corresponds to a hexagonal Co_2O_3 -like structure with tetrahedral coordination of the Co atoms whereas c-CoO phase is stable for the other oxide substrates, although slightly distorted due to lattice mismatch [4]. These propositions can be examined by using the present XAS spectra and further work is in progress to validate these assignments. Similarly, detailed ab initio calculations are in progress to determine the occurrence of cross-linking-bonds of the form Co-O-M, where M stands by Si, Al and Mg atoms, at the interface, as previously reported for similar NiO systems.

References:

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