



	Experiment title: Local atomic structure at the interface between cerium oxide and Pt(111)	Experiment number: 08-01 921
Beamline:	Date of experiment: from: 05/09/2011 to: 09/09/2011	Date of report: 21/08/2012
Shifts:	Local contact(s): Francesco D'Acapito	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Paola Luches* Federico Boscherini* Sergio Valeri* Federico Pagliuca*		

Report:

We performed a study of the structure of cerium oxide ultrathin films supported on Pt(111), focused on the evolution of the epitaxial strain in films of different thickness. The basis for the experiment was provided by our previous in-house structural and compositional characterization of the same system, which showed that stoichiometric CeO₂ films with flat terraces and a good epitaxial quality can be obtained [1]. With the present experiment we aimed at determining the precise epitaxial relation between cerium oxide and the Pt substrate, given the considerable lattice mismatch (38%) between the two materials in the bulk phase, and to determine the presence and origin of possible strains in the film.

In the experiment here described we measured two cerium oxide samples of 2 and 10 ML thickness. The samples were grown in a UHV apparatus located in our laboratories, using the procedures described in [1], and they were kept in a non-reactive atmosphere during their transfer to the synchrotron radiation laboratory. The XAS measurements at the Ce L₃ absorption near edge (x-ray absorption near edge spectroscopy XANES) and extended energy region (x-ray absorption fine structure - XAFS) were performed at the Italian CRG GILDA BM08 beamline. We exploited the polarization dependence of the XAFS cross section by changing the relative orientation between the sample normal and the polarization of the impinging x-ray beam in order to preferentially probe either the in-plane or the out-of-plane atomic correlations. In particular, we used two experimental configurations: the spectra indicated as PER are measured with the sample in vertical position, with the photon beam at 20° from the sample surface and the electric vector at 20° from sample normal; the spectra indicated as PAR are measured with the sample in horizontal position, with the photon beam at a few degrees from the sample surface and the electric vector along the surface plane. All spectra from the films were acquired in the fluorescence yield mode. Besides the two cerium oxide films, a standard sample made of CeO₂ powder, i.e. with Ce formally in the 4+ oxidation state, and a cerium silicate film with Ce in the 3+ oxidation state were also measured for comparison. The CeO₂ powdered sample was measured in the transmission mode, while the silicate film was measured in the fluorescence yield mode in the PER

configuration. The XAFS data analysis was performed using the theoretical scattering amplitudes and phase shifts generated by the FEFF code.

Due to the presence of an unavoidable, though small, Cr-K adsorption edge signal – probably originating from diffused light scattering from the chamber walls – we had to limit the measured spectra to 5980 eV photon energy. Fig. 1 shows the Fourier transforms of the k^2 -weighted $\chi(k)$ and the relative first-shell fits in the PAR and PER configurations, together with one of the $\chi(k)$, to give an idea of the high quality of the data. The value of S_0^2 was determined from the fit of the CeO_2 reference sample and kept fixed for the fitting of the four spectra of the films. The good quality of the fits of the spectra measured on the films indicates that also in the ultrathin limit of a few atomic layers the local structure of cerium oxide is the fluorite one. The fits of the 10 ML spectrum in the PAR and PER configurations result in a first neighbor distance slightly contracted with respect to the bulk value. The contractions are more pronounced in the case of the 2 ML film in both PAR and PER experimental configurations.

The driving force for the observed contraction is probably the presence of the Pt substrate, which forces the cerium oxide film, at least at the early stages of the growth, to adopt an in plane compression to match the substrate with a $3 a_{\text{CeO}_2} : 4 a_{\text{Pt}}$ coincidence. The films result expanded out-of plane following the bulk elastic constants even at low dimensionality. The epitaxial compression is partially relaxed at 10 ML.

This work, establishing the exact epitaxial relation between the ceria film and the Pt substrate and giving an accurate evaluation of the ceria film structure, provides a basis for further studies of systems based on these films, e.g. as supports for metal nanoparticles. A paper based on these results is in preparation.

[1] P. Luches, F. Pagliuca, S. Valeri, J. Phys Chem C 115, 10718 (2011).

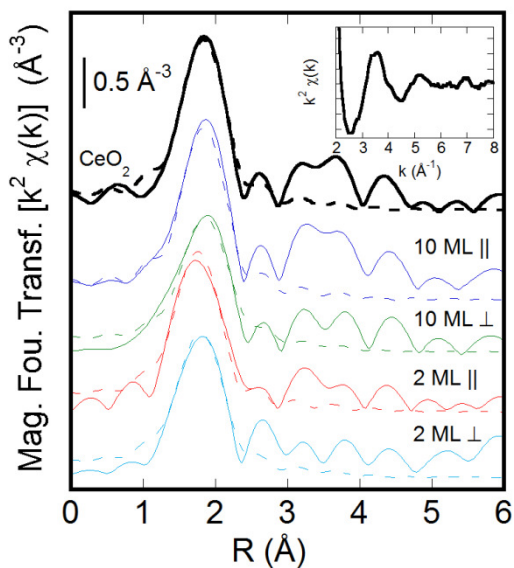


Fig.1: Modulus of the Fourier transform of the k^2 -weighted Ce L_3 edge $\chi(k)$ (solid lines) and first shell fits (dashed lines) for the CeO_2 standard sample and for the 10 ML and 2 ML CeO_2 films in the PAR and PER geometry. The inset shows the Ce L_3 edge $\chi(k)$ data for the 2 ML sample.