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Names and affiliations of applicants (* indicates experimentalists):

Paola Luches*[1], Francesco Benedetti*[1,3], Jacopo Stefano Pelli Cresi*[1,3], Francesco Carla[4] Lucia Amidani*[4], Federico Boscherini*[5,6]

[1] Centro S3, Istituto Nanoscienze, Consiglio Nazionale delle Ricerche, Modena, Italy

[2] Department of Chemical and Geological Sciences, University of Modena and Reggio Emilia, Modena, Italy

[3] Department of Physical, Information and Mathematical Sciences, University of Modena and Reggio Emilia, Modena, Italy

[4]European Synchrotron Radiation Facility, BP 220, F-38043 Grenoble, France

[5]Dipartimento di Fisica e Astronomia, Università di Bologna, Viale C. Berti Pichat 6/2, 40127 Bologna, Italy

[6]Operative Group in Grenoble, Istituto Officina dei Materiali, Consiglio Nazionale delle Ricerche, c/o ESRF, BP 220, F-38043, Grenoble, France

Report:

The aim of the experiment was to investigate the evolution of the structure of cerium oxide ultrathin films of different thickness supported on a Pt(111) single crystal during reduction and oxidation treatments. This goal was achieved by surface X-ray diffraction (SXRD) and X-ray reflectivity (XRR) measurements during thermal treatments in oxidizing and reducing atmoshpere.

The samples investigated were two CeO_2 ultrathin epitaxial films of different thickness (2 ML and 4 ML) supported on Pt(111) single crystals. The samples were grown by MBE in our home laboratories and carried to the ESRF in non-reactive atmosphere.

Each sample was subject to the following treatments in the UHV chamber of the experimental hutch 2: i) a first cleaning procedure by mild annealing in O_2 partial pressure (T = 400°C, $P_{O_2} = 1\times10^{-7}$ mbar) to remove carbon contamination due to air exposure; ii) reducing thermal treatments at increasing temperature in UHV in the 400- 750º C range. Only for the 2 ML sample a re-oxidizing treatment at 600º C in an O_2 pressure of 1×10^{-7} mbar was also performed. The samples were kept at each temperature step for 30 minutes and cooled down to room temperature before the measurements.

The incident photon beam, with energy of 24 keV, was focused on the sample surface at grazing incidence. A horizontal geometry z-axis diffractometer with a position sensitive detector was used for data acquisition.

The structure of the samples after each temperature step was analysed by measuring X-Ray Reflectivity (XRR), SXRD (h,k) reciprocal space maps at l = 0 and l = 0.72 (l=1 in the CeO_2 reciprocal space), and cerium oxide and Pt Crystal Truncation Rods (CTR) at different (h,k) values. Moreover, Auger electron spectroscopy was used to check the evolution of the sample surface composition at each temperature step.

The (h,k) reciprocal space maps for different l values acquired on the 2 ML sample after the cleaning procedure are characterized by different periodicities: one is compatible with the Pt(111) surface structure, a second one is ascribed to the CeO_2(111) lattice (1.4 times larger with respect to the Pt one). Moreover, ±5º rotated CeO_2 domains are evident on the surface (Fig.1a). The XRR curves show significant modifications after the reduction

treatment (Fig.2). Some slight modifications of the in plane CeO_2 periodicity could be observed also in the reciprocal space maps acquired at the different reducing steps. Remarkably, a new periodicity with respect to the Pt spots appears on the 2 ML sample after the thermal treatment at 600° C in UHV (Fig.1b). The new structure is evident also at $l > 0$, and it persists after the treatment at 750°C. Also the 4 ML sample exhibits similar structural modifications, although the (2×2) phase appears at a slightly higher temperature (650° C). All of the observed structural modifications are reversible: the original surface structure can be re-obtained after the oxidizing thermal treatment. A detailed analysis, including the simulation of XRR curves and CTR, is being performed in order to assign the observed periodicities to the correct structural phases.

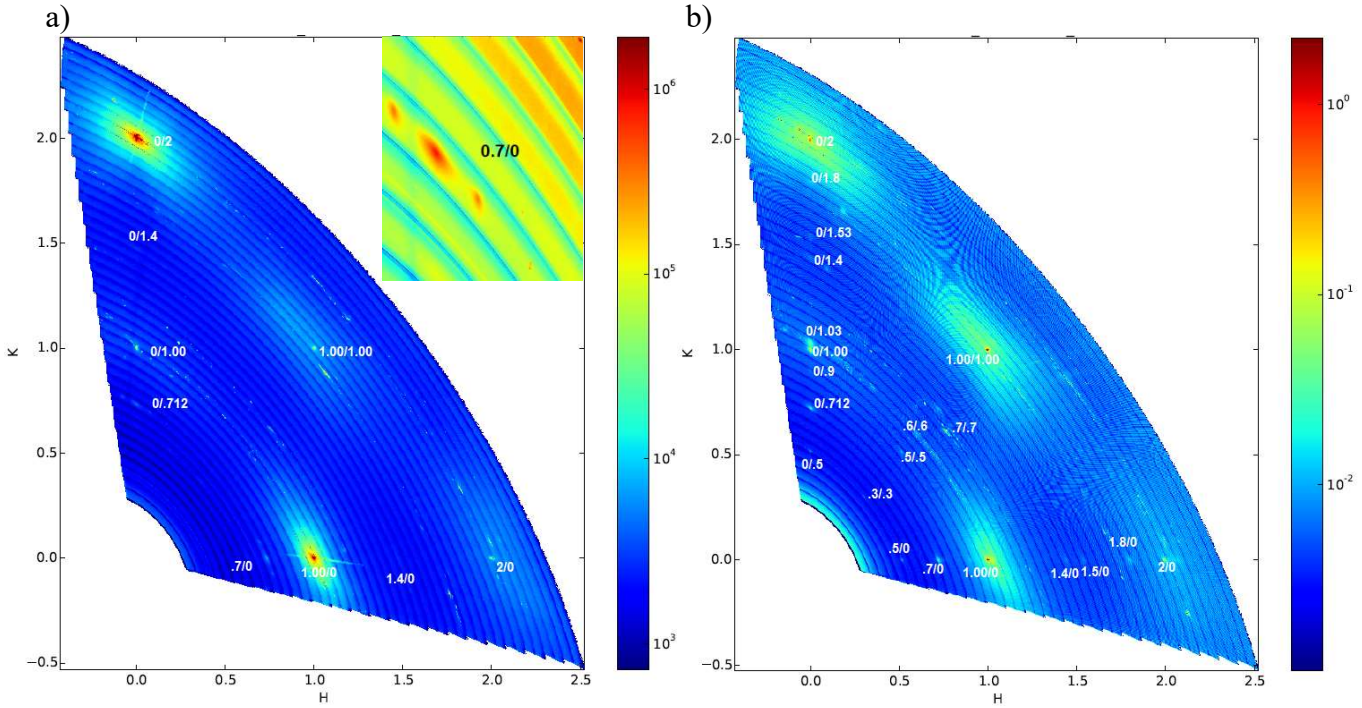

Fig.1: (h,k) reciprocal space maps at $l = 0$ of the 2 ML cerium oxide film (a) after the cleaning treatment (the inset shows a zoom of the (0.7,0) region) and (b) after a reducing treatment in UHV at 600°C.

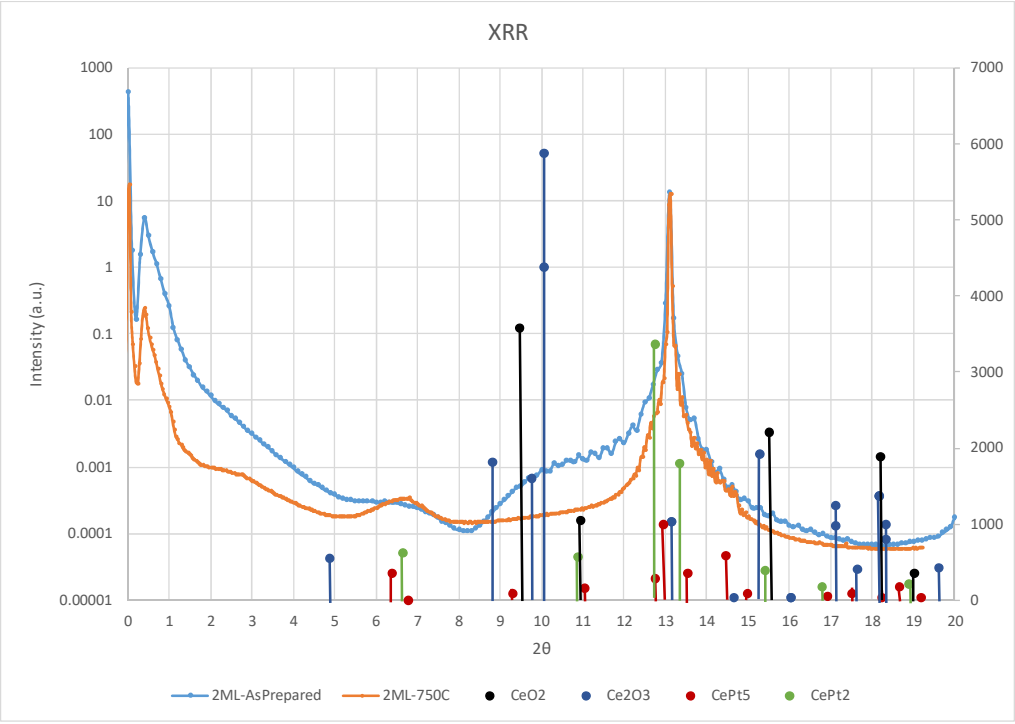

Fig. 2: XRR curves of the 2 ML cerium oxide film after the cleaning treatment (blue line) and after a reducing treatment in UHV at 750°C (orange line). The vertical lines correspond to powder X-ray diffraction peaks of different cerium oxide and Ce-Pt alloy structures.