Characterising ultrathin ceria films at the nanoscale: Combining spectroscopy and microscopy

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ABSTRACT

$CeO_{2-x}(1\,1\,1)$ ultrathin films consisting of small, discrete islands decorating a $Pt(1\,1\,1)$ substrate have been studied using a combination of Scanning Tunnelling Microscopy, Low-Energy Electron Microscopy, and Low-Energy Electron Diffraction. Significantly, the chemical nature of the ceria film has also been probed using X-ray Absorption Spectroscopy (XAS) combined with X-ray PhotoEmission Electron Microscopy (XPEEM) in the same ultrahigh vacuum system. XAS spectra over the Ce M_5 absorption edge demonstrated that the ceria islands contained ∼50% Ce^{4+} and ∼50% Ce^{3+}, leading to an overall stoichiometry of $CeO_{1.75}$, which was uniform across the film. The unique advantage of this experimental setup is the application of multiple techniques on the same sample: high-resolution STM to monitor the morphology, XPEEM to probe the stoichiometry, and LEEM to act as a bridge between the two.

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1. Introduction

Ceria-based heterogeneous catalysts have been the focus of much research over the past decade due to their numerous applications across a range of processes [1]. Lately, attention has focussed on understanding the mechanisms behind the catalytic activity, especially with regards to interactions with metal nanoparticles. One key characteristic of ceria is its oxygen storage and release ability, due to the facile inter-conversion between the Ce^{3+} and Ce^{4+} oxidation states. In order to facilitate the study of these oxide nanostructures, ultrathin oxide films are normally grown on noble metal supports such as $Pt(1\,1\,1)$. This approach also overcomes the charging problem encountered when applying electron-based experimental techniques to insulating oxides such as ceria. This arrangement, when using a catalytically relevant metal substrate has been termed an "inverse model catalyst" and also permits the investigation of the interaction between the support and the oxide film in certain cases. To this end, $CeO_2(1\,1\,1)$ films have been prepared on a number of substrates including $Pt(1\,1\,1)$ [2,3], $Ru(0\,0\,0\,1)$ [4–6], $Rh(1\,1\,1)$ [7,8], $Au(1\,1\,1)$ [9,10], and $Cu(1\,1\,1)$ [11,12], and probed with a wide range of techniques.

Low-Energy Electron Microscopy (LEEM) and synchrotron-based X-ray PhotoEmission Electron Microscopy (XPEEM) have been employed to great effect in order to investigate many different phenomena on metal nanostructures supported on metal oxides [13,14]. Recently, these techniques have also been applied to the study of ultrathin $CeO_2(1\,1\,1)$ films on $Cu(1\,1\,1)$ [15], $Ru(0\,0\,0\,1)$ [6,16] and $Re(0\,0\,0\,1)$ [17]. The high lateral resolution of LEEM coupled with the chemical sensitivity of XPEEM is a powerful tool to investigate the morphology and growth of such films and the application of localised spectroscopic measurement aids in separating the effects of the substrate from those of the ceria nanostructures.

Due to its position as the primary high-resolution real-space technique for the surface morphology of many materials, Scanning Tunnelling Microscopy (STM) is commonly used in the preparation of samples prior to spectroscopic measurements. When considering synchrotron-based experiments such as those requiring resonant photoemission spectroscopy (ResPES) or X-ray Absorption Spectroscopy (XAS), this often means that the thin films are initially characterised ex situ using STM and then either transported to a synchrotron beamline under inert conditions or prepared again at the beamline. Since the preparation conditions, especially the annealing temperature, are critical for many metal oxide surfaces there are inevitably some variations in the film quality [18]. It is

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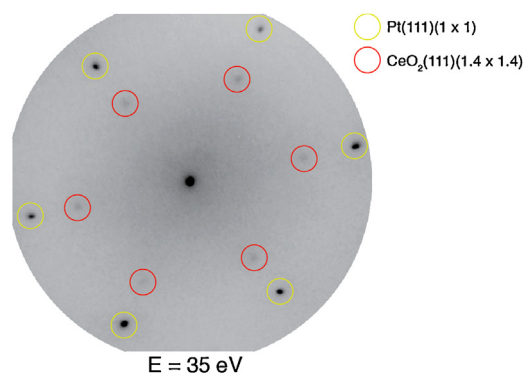   E-mail address: g.thornton@ucl.ac.uk (G. Thornton).

also common to carry out post-analysis of the thin films by transporting them to the home laboratory under an inert gas such as argon or nitrogen. However, even a small amount of contamination may induce changes to the structure of the films, especially on the lengthscales probed with high-resolution probes such as STM. The possibility of carrying out in situ STM in combination with X-ray measurements (XPEEM), without breaking UHV conditions, is therefore a clear advantage. In this work, we examine the potential for such measurements using the results of investigations on ultrathin $CeO_{2-x}(1\,1\,1)$ films on $Pt(1\,1\,1)$ as an example. The results point to the formation of hollow $CeO_{2-x}(1\,1\,1)$ islands as identified with STM and LEED, with a uniform stoichiometry of $CeO_{1.75}$ from spectroscopic XPEEM measurements.

2. Experimental procedure

Synchrotron experiments were conducted at the Nanoscience beamline (I06) situated at the Diamond Light Source (Oxfordshire, UK), using an Elmitec SPELEEM-III microscope. This instrument is capable of performing LEEM and XPEEM with lateral resolutions of 20 nm and 50 nm, respectively. XPEEM spectro-microscopy provides chemical sensitivity either via X-ray absorption or photoemission, the latter with an electron energy resolution of ~150 meV. Attached to the main chamber is a preparation chamber containing facilities for LEED and Auger electron spectroscopy (AES) as well as standard sample preparation facilities and an *Omicron* variable-temperature scanning tunnelling microscope (VT-STM). A specially adapted sample carrier was employed, capable of housing an *Omicron*-compatible Mo sample plate within an *Elmitec* cartridge.

The $CeO_2(1\,1\,1)$ ultrathin films were prepared on a $Pt(1\,1\,1)$ surface using a post-oxidation procedure, as detailed elsewhere [2]. The $Pt(1\,1\,1)$ substrate was prepared by multiple cycles of Ar^+ ion-sputtering and annealing in UHV to ~1100 K until a sharp (1×1) LEED pattern was observed and the contamination was below the detection limit of AES. 0.5 ML Ce metal (99.9%, Alfa Aesar) was deposited onto the clean $Pt(1\,1\,1)$ surface at room temperature from a *Focus* EFM-3 evaporator. The thin film was subsequently

annealed to 900 K in UHV to form a Pt/Ce surface alloy, characterised by a $(2 \times 2)R30°$ LEED pattern relative to $Pt(1\,1\,1)(1 \times 1)$. This was followed by annealing to 900 K in 5×10^{-7} mbar O_2 to form an epitaxial $CeO_2(1\,1\,1)$ film with LEED reflexes at (1.4×1.4) relative to the substrate. The structure of the film was investigated with STM prior to the synchrotron radiation measurements. The ceria coverage is given as a monolayer equivalent (MLE), which was determined using STM. One monolayer is defined as the complete coverage of the substrate by a single CeO_2 trilayer (corresponding to a thickness of 0.31 nm). The temperature during film preparation was monitored using an optical pyrometer. Photon energies were calibrated to the Ce M_5 absorption edge for Ce^{4+} at 883.8 eV.

3. Results and discussion

The LEED pattern from a typical $CeO_{2-x}(1\,1\,1)$ film is presented in Fig. 1. The hexagonal lattice of the $Pt(1\,1\,1)(1 \times 1)$ is highlighted in yellow, whereas the spots from the epitaxial $CeO_{2-x}(1\,1\,1)$ film are highlighted in red. There is no evidence of rotational domains of the ceria, in contrast to films formed on $Re(0\,0\,0\,1)$ [17], $Ru(0\,0\,0\,1)$ [5]
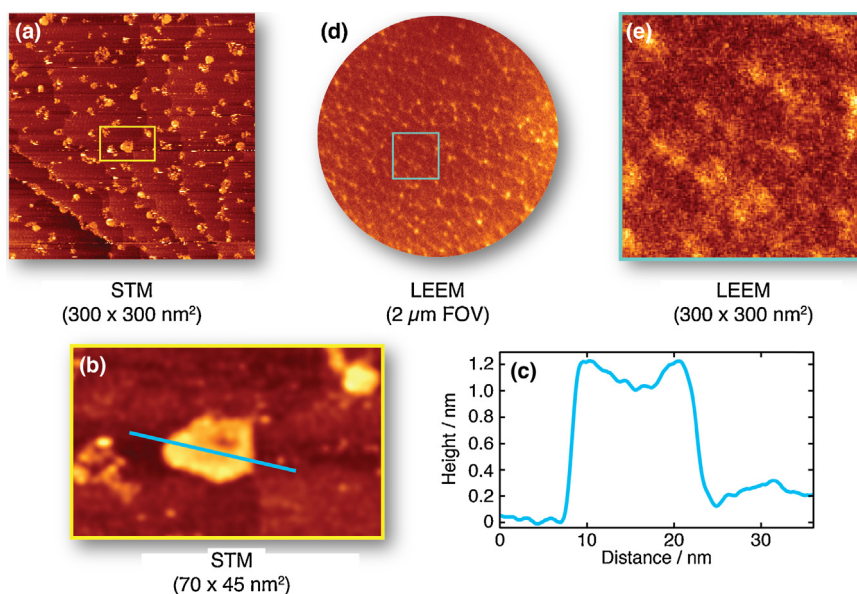
Fig. 2. LEEM and STM images of the $CeO_{2-x}(1\,1\,1)$ film on $Pt(1\,1\,1)$. (a) Large-scale STM image (300 nm × 300 nm, $V_s = +2.2$ V, $I_t = 0.1$ nA) obtained prior to examination with LEEM. (b) Expanded view of the area in (a) highlighted with a yellow rectangle, displaying one of the larger ceria islands. (c) Line profile obtained across the large ceria island shown in (c) indicated with a blue line. (d) MEM (Mirror Electron Microscopy) LEEM image (2 μm field of view, $E = 0.45$ eV) of the ceria film. (e) Expanded view of the 300 nm × 300 nm region bordered by the light-blue square in the LEEM image in (d) (For interpretation of the references to color in this figure legend, the reader is referred to the web version of the article.).