Annealed CeO$_2$/hex-Pr$_2$O$_3$/Si(111) multilayer systems

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Combining cerium and praseodymium oxides is a promising approach to engineer catalysts with tailored reactivity and selectivity by improving the characteristics of the catalyst, e.g. oxygen storage capacity (OSC), oxygen mobility, and thermal stability [1]. Prepared as single-crystalline thin oxide films on plane substrates, they also can be used as model catalyst systems [2]. Here, we report about the surface morphology and structure of CeO$_2$(111)/hex-Pr$_2$O$_3$(0001)/Si(111) multilayer systems, which are of interest as a model catalyst for CeO$_2$ with enhanced oxygen storage capacity by charging and discharging the buried hex-Pr$_2$O$_3$ layer.

Ultra thin hexagonal Pr$_2$O$_3$ films (thickness 3 nm) were deposited on boron doped Si(111) substrates using a standard procedure [3]. Afterwards crystalline ceria films of 180 nm film thickness were grown on these support systems via MBE at 625°C substrate temperature [4]. The surface morphology of the CeO$_2$(111)/hex-Pr$_2$O$_3$(0001)/Si(111) multilayer systems was studied under annealing conditions up to T = 500°C by in situ AFM and SPA-LEED measurements at a base pressure of p < 10$^{-10}$ mbar. Furthermore, in situ XRR and XRD measurements (p < 10$^{-6}$ mbar) of untreated and annealed samples (T = 500°C) were performed at room temperature in order to study structural changes of the whole multilayer system. These experiments were done at beamline W1 at HASYLAB using a home-made UHV babychamber and a six circle diffractometer with horizontal alignment. The energy of the x-ray beam was 10.5 keV.

Figure 1(a) shows an exemplary AFM image of the ceria film surface after annealing at T = 500°C. No atomic resolution was achieved, but regular pyramidal structures with identical orientation can be observed. The height of the structures is approximately 7 nm and the base length results to 100 nm. These structures always occur for lower annealing temperatures (images not shown here). Additional bright spots corresponding to needle-like structures can be seen in Fig. 1 (a) which only emerge in the temperature region of T = 250°C–500°C. The SPA-LEED diffraction pattern (E$_{el}$= 116 eV) shown in Fig. 1 (b) points to a surface structure with 3-fold symmetry according to CeO$_2$(111) (fcc-structure). Nevertheless, the (00)-spot has a star-like shape with 3-fold symmetry and sophisticated spot profile analysis reveals that it consists of a central peak with three satellites nearby (cf. inlet in Fig. 1(b)). This agrees well with the AFM studies assuming the pyramidal structures to be faceted.

XRR measurements of the untreated sample and after annealing at T = 500°C are shown in Fig. 1 (c). Here, the small and broad intensity oscillations are due to the ceria film and the praseodymia buffer layer, respectively. The film thickness can be calculated from the period lengths and it can be observed that the film thickness of the ceria film (180 nm) is stable under annealing conditions. However, the thickness of the buffer layer seems to decrease due to interface effects like oxygen transfer and subsequent Pr-silicate formation [5].

The XRD measurements of the specular crystal truncation rod (CTR) close to the Bragg condition L=1 (L in Si(111) surface coordinates) are shown in Fig. 1(d). In both measurements a sharp Bragg peak due to the Si substrate can be seen as well as an additional broader Bragg peak at higher L values caused by the crystalline ceria film. The position of these peaks corresponds well with the literature bulk value of CeO$_2$(111). Furthermore, additional broad oscillations (fringes) with low intensity can be observed due to the crystalline praseodymia buffer layer. After annealing at T= 500°C an additional spot emerges at lower L values compared to the Si Bragg peak position pointing to the formation of another oxide species. Whereas, the peak position is near the literature bulk value of Ce$_2$O$_3$(111) it exhibits a significant shift to higher L values (+1 %) which is maybe due to strain effects. Finally the intensity oscillations due to the buffer layer is damped after annealing caused by an interface roughening of the praseodymia film.
In summary, we have shown that the surface morphology of ceria films on hex-Pr$_2$O$_3$(0001)/Si(111) support systems is stable under annealing conditions except the agglomeration of small needle-like structures. However, significantly changes of the structure within the multilayer system can be observed regarding the formation of an additional oxide species and the roughening of the hex-Pr$_2$O$_3$ buffer layer.

Figure 1: (a) and (b) AFM image and SPA-LEED pattern (E$_{el}$=116 eV) of the ceria film surface after annealing at 500 °C. (c) and (d) XRR measurements and specular CTRs at $L \approx 1$ of the untreated (black line) and the annealed sample (red line). In (d) expected positions for bulk CeO$_2$ and bulk Ce$_2$O$_3$ are indicated.

References