Nanoscale analysis of the oxidation state and surface termination of praseodymium oxide ultrathin films on ruthenium(0001)

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ABSTRACT

The complex structure and morphology of ultrathin praseodymia films deposited on a ruthenium(0001) single crystal substrate by reactive molecular beam epitaxy is analyzed by intensity-voltage low-energy electron microscopy in combination with theoretical calculations within an *ab initio* scattering theory. A rich coexistence of various nanoscale crystalline surface structures is identified for the as-grown samples, notably comprising two distinct oxygen-terminated hexagonal $Pr_2O_3(0001)$ surface phases as well as a cubic $Pr_2O_3(111)$ and a fluorite $PrO_2(111)$ surface component. Furthermore, scattering theory reveals a striking similarity between the electron reflectivity spectra of praseodymia and ceria due to very efficient screening of the nuclear charge by the extra 4*f* electron in the former case.

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1. Introduction

Metal oxide surfaces and thin films are almost ubiquitously found in solid state nanoscience and technology, ranging from applications in microelectronics as integral parts of field effect transistors in complementary metal-oxide-semiconductor technology to functional coatings in tribology and sensing as well as active support materials in heterogeneous catalysis. To determine their specific role in any of these fields of application, a detailed understanding of the fundamental structural (geometric) properties of the oxide films is key to understanding their physical, chemical, and materials properties, which in turn govern their interaction with their surrounding or give rise to their specific funtionality. Owing to the structural heterogeneity that is frequently found in the materials employed, a microscopic approach to unraveling the (local) structure and spatial distribution of the oxide is often required. This is even more so when the problem demands a de-

scription on different length scales, *e.g.*, of the elemental interactions on an atomic scale and diffusive processes over mesoscopic to macroscopic distances, which is a situation typically encountered in heterogeneous catalysis.

Low-energy electron microscopy (LEEM) [1] is a surface science technique that combines full-field diffractive imaging with ultrahigh vacuum compatibility and surface sensitivity. The latter is ensured by using slow electrons impinging on the sample surface typically at normal incidence and kinetic energies from about 0 eV up to a few tens of eV, which depending on electron energy, geometric and electronic structure gives rise to strongly backscattered electron beams [2]. Owing to the diffractive nature of the electron-sample interaction and the underlying scattering processes, the energy-dependent reflected beam intensity, *i.e.*, the so-called intensity-voltage ($I(V)$) curve of the (00) beam in conventional low-energy electron diffraction (LEED) nomenclature, may comprise intensity modulations that are characteristic of the illuminated material and its particular geometric and electronic structure [3]. The dependence on surface geometric and electronic structure has also been shown for the related, earlier developed very-low-energy electron diffraction (VLEED) technique

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and also found in theoretical approaches to understand the problem of electron reflectance spectra from crystalline surfaces [4–7]. Consequently, in bright-field imaging mode this $I(V)$ dependence determines the local electron reflectivity and represents the corner stone of amplitude contrast formation for heterogeneous samples.

A few years ago, we have demonstrated that local $I(V)$ analysis performed in bright-field LEEM is capable of identifying the structure of atomically thin transition metal oxide films, e.g., of NiO [8] and few-nanometer thin films of cerium oxide of different oxidation state [9–11]. Local $I(V)$ analysis has also been employed in a fingerprinting mode to distinguish between various forms of iron oxide [12–15]. Yet, due to an extended probing depth at very low electron energies a rather contentious topic is the question whether $I(V)$-LEEM is also able to distinguish between different terminations of the oxide, which may possibly coexist after preparation in addition to different oxidation states. Recently, we have provided evidence that $I(V)$-LEEM is able to discriminate between various submonolayer coverages between one quarter to a full monolayer of chemisorbed oxygen on Ru(0001) [16].

Here, we analyze the reflectivity spectra of ultrathin praseodymium oxide films grown on a Ru(0001) surface, which we have very recently shown to initially form large, regular shaped oxide islands that sequentially thicken in a layer-by-layer fashion at a later stage [17]. We showcase that, in perfect analogy to cerium oxide [10], we can distinguish between the different crystallographic structures (hexagonal (a)-Pr_2O_3, cubic (c)-Pr_2O_3, and (fluorite) PrO_2) representative of the different valence states (Pr^{3+}, Pr^{4+}) for the praseodymium cations [18], and we will show that our method even allows distinguishing and determining the local type of oxide termination within the same oxidation state and crystal structure.

2. Material and methods

The experiments were performed in two separate commercial Elmitec LEEM III systems, one installed at the University of Bremen, Germany and the other at beamline I311 of the MAX-lab synchrotron radiation facility in Lund, Sweden. The latter system is additionally equipped with an energy filter enabling operation as a spectroscopic photoemission and low-energy electron microscope (SPE-LEEM), employing low energy electrons from the internal electron gun or photoelectrons excited by the incident synchrotron radiation in a photon energy range of about 43–1500 eV. Both operation modes have been used for extensive characterization of the praseodymia growth on Ru(0001) in a previous study [17]. Briefly, the Ru(0001) single crystal (Mateck) was cleaned *in situ* using established procedures, involving repeated oxidation and high-temperature annealing as described elsewhere [19,20]. Sequentially, praseodymium oxide was deposited *in situ* by reactive molecular beam epitaxy (MBE) involving evaporation of metallic Pr onto the clean Ru(0001) substrate at 760 °C in a molecular oxygen partial pressure of 5×10^{-7} Torr. Oxide island thicknesses were determined by *ex situ* atomic force microscopy (AFM).

In the present article, we concentrate on the detailed analysis of the accompanying $I(V)$-LEEM data that were acquired for the same samples as presented in the growth study [17]. In contrast to previous $I(V)$-LEEM studies of similar systems, the $I(V)$ curves were collected with an energy slit in the dispersive plane of the energy analyzer of the microscope in Lund (effective energy resolution about 0.3 eV), resulting in enhanced image contrast and visibly sharper features in the $I(V)$ spectra than in our LEEM III system without energy filter. While both effects are most prominent at very low energies, e.g., near the transition to the mirror mode, the main part of the $I(V)$ curve is only weakly affected.

3. Results and discussion

This section is organized as follows: In Section 3.1, we present characteristic $I(V)$ curves for flat praseodymia films and recap important results from the previous growth study [17], thereby introducing the most prominent crystallographic structures of bulk praseodymia. The theoretical methodology for the calculation and interpretation of the electron reflectivity spectra of praseodymia surfaces is laid out in Section 3.2, which also includes a comparison to ceria, the neighboring lanthanide. The following Section 3.3 is devoted to the comparison between calculated spectra and experimentally available data, facilitating an identification of the distinct structural components of the oxide film. Finally, based on the structural identification obtained, we apply the $I(V)$-LEEM fingerprinting methodology to obtain a quantitative mapping of the praseodymia surface composition with spatial resolution in the low nanometer range (Section 3.4) and discuss the structural implications for the praseodymia-ruthenium system.

3.1. Intensity-voltage analysis of praseodymia films on Ru(0001)

A representative LEEM image of the praseodymia film grown on the Ru(0001) surface is displayed in Fig. 1(a). From the *in situ* observations during growth [17] in combination with spatially resolved X-ray absorption spectroscopy (XAS) data recorded in photoemission electron microscopy (XAS-PEEM) mode, the bright regions were attributed to substrate regions that are not covered by praseodymia. The oxide islands have evolved along the substrate steps and step bunches, which run from the top toward the bottom edge of the image. Yet, $I(V)$ analysis readily reveals these surface regions to be composed of a chemisorbed monolayer of oxygen within a (1×1)-O structure [16,20]. However, the areas attributed to the praseodymia islands exhibit *five* distinct $I(V)$ curves as shown in Fig. 1(b), which is indicative of a non-homogeneous composition of the oxide film. To enable a structural interpretation of the $I(V)$ data, the present state of knowledge for praseodymia growth on ruthenium will briefly be summarized.

In the previous study [17], based on XAS-PEEM, the oxidation state of the praseodymia islands was largely identified as Pr^{3+} whereas a substantial contribution of Pr^{4+}, which is representative of the fluorite crystal structure (see Fig. 2(a)), was discarded. Furthermore, together with micro-illumination low-energy electron diffraction (μLEED) the associated crystal structure was identified as the hexagonal sesquioxide $Pr_2O_3(0001)$ with two different registries to the underlying ruthenium, one in which the surface lattice is collinear with the substrate lattice (only found for in highly stepped substrate regions) and one in which the surface lattice is azimuthally rotated by $\pm11.5°$. The existence of the c-Pr_2O_3 phase, also known as the bixbyite structure, was ruled out due to the absence of the closely spaced diffraction spots representative of the (4×4) surface periodicity with respect to the fluorite structure (cf. Fig. 2(b) for details). Moreover, the contrast observed in dark-field LEEM using the praseodymia integer beams was tentatively explained by the existence of two different surface terminations of the $Pr_2O_3(0001)$ film separated by an atomic step about 3 Å high, which corresponds to half the height of the bulk unit cell of the hexagonal crystal structure. Moreover, the six-fold symmetry of the bulk is broken at the surface, as also illustrated in Fig. 2(c).

Due to the structural similarity between the two lanthanides cerium oxide and praseodymium oxide, it is quite reasonable to approach the problem of $I(V)$ analysis for praseodymia by comparing to the known $I(V)$ curves for cerium oxide, which are already quite well understood based on calculation using *ab initio* scattering theory [10]. Intriguingly, closer inspection of Fig. 1(b) indeed reveals a striking similarity between the $I(V)$ curve associated with the praseodymia island edges and the $I(V)$ spectrum from fully ox-