a) Title

Stoichiometry-structure correlation of epitaxial $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0-1$) thin films on Si(111)

b) Authors

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d) Abstract

Epitaxial oxide thin film layers are of interest for model catalytic studies. We report the growth of $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ mixed oxide layers of different stoichiometries ($x = 0-1$) and oxygen deficiency ($\delta > 0$) on Si(111) by co-evaporating molecular beam epitaxy. The main objective is to identify the crystal phases and to investigate the correlation between compositions and

crystal structures. X-ray photoemission spectroscopy was performed to quantify the stoichiometries. An extensive laboratory and synchrotron based X-ray diffraction analysis was carried out to determine the vertical and lateral lattice orientations and the strain status of the layers. The study revealed that single crystalline $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}/\text{Si}(111)$ heterostructures can be epitaxially grown on Si(111) for model catalytic studies. In addition to the structure-stoichiometry relationship typical to mixed oxide bulk powders, we identified a hexagonal mixed Ce-Pr oxide thin film phase not yet reported in bulk studies.

e) Keywords

A1. X-ray diffraction, A1. Crystal structure, A3. Molecular beam epitaxy, B1. Oxides, B1. Rare earth compounds

f) Main text

1. Introduction

Cerium oxide has been studied for several applications, e.g. high-k material, silicon-on-insulator buffer layer and solid oxide fuel cells [1-3]. In terms of catalysis cerium oxide is of interest for oxidative dehydrogenation, oxidative coupling, methane conversion, water-gas shift reaction and three-way catalysis [4-8]. To gain a microscopic insight into this processes, model catalytic surface science experiments are a valuable approach [9-11]. It is noted that this approach has already been successfully applied to pure cerium oxide [12]. In particular, $\text{CeO}_2(111)$ films were grown on Si(111) exhibiting a fluorite lattice [13,14]. Recently, ultrathin Ce_2O_3 films were successfully stabilized under UHV condition on Si(111) [15]. Furthermore, CeO_2 surface science model catalysis was applied in terms of temperature induced reducibility and chemisorption of different gases (CO , NO , H_2) [16-19]. It was found that the catalytic reactivity of CeO_2 surfaces is based on a complex interaction between the educts and the lattice oxygen, accompanied by a $\text{Ce}^{3+}/\text{Ce}^{4+}$ valence state variation [20].

Interestingly, the neighbouring rare earth oxide, praseodymium oxide, is also known for its catalytic activity [21,22]. However, far less model catalysis studies in surface science were devoted to this system, due to its extremely complex Pr-O phase diagram [23]. Rather recently, the growth of various praseodymium oxide phases in the form of single crystalline films on a support system became feasible. Pure praseodymium oxides were for example grown on Si(111) substrates for microelectronic applications [24,25]. Under UHV oxygen deficient conditions, praseodymium prefers the Pr^{3+} state and the hexagonal (0001) oriented (hex) Pr_2O_3 lattice on Si(111) [24-28]. A preparation method was found to induce a phase transformation from hex- Pr_2O_3 (0001) films to single crystalline cubic (cub) Pr_2O_3 (111) films on Si(111) [29,30]. As the bixbyite cub- Pr_2O_3 bears a close crystallographic relationship to the fluorite PrO_2 phase, the preparation of the later phase became possible by oxygen treatment [31,32]. The availability of single crystalline cub- Pr_2O_3 (111) and PrO_2 (111) films on Si(111) offers thus the opportunity to study catalytic redox reactions by surface science, including the Pr_6O_{11} phase, which exhibits the highest oxygen exchange activity among all rare-earth oxides (REO) [33].

Mixing cerium and praseodymium oxide enables to engineer further important catalytic properties, such as oxygen mobility and oxygen storage capacity (OSC) [34-36]. Thus, the growth of single crystalline $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0-1$) films is expected to expand the parameter space for model catalysis surface science studies, benefiting from the very different redox activity of $\text{Ce}^{4+}/\text{Ce}^{3+}$ ($E^0 = +1.7$ V) and $\text{Pr}^{4+}/\text{Pr}^{3+}$ ($E^0 = +3.2$ V) [37]. However, no growth study of epitaxial $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0-1$) mixed oxide thin-films on support substrates is known in the literature, but polycrystalline mixed oxide powders were prepared by the sol-gel method or by hydrothermal combustion of RE nitrates [34-36]. In particular, McCullough investigated the lattice constant as a function of the stoichiometry for mixtures of CeO_2 and Pr_2O_3 [38]. Thereby, a linear behaviour called Vegard's law turned out for an rare earth atomic concentration lower than 50% of Pr in the CeO_2 based mixed oxide fluorite phase. A bixbyite

phase was observed for higher than 85% of Pr. In between these Pr concentrations both phases were found. However, no observation of any hexagonal Ce-Pr mixed oxide phase was reported.

The main objective of the current work is to establish $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0-1$) mixed oxide thin-films on Si(111) as an appropriate heteroepitaxial system for model catalytic studies. For this purpose, $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}/\text{Si}(111)$ heterostructures of three different stoichiometries were grown by co-evaporating MBE. An extensive analysis using x-ray diffraction and x-ray photoelectron spectroscopy was carried out to correlate the crystal structures with the stoichiometries and valence states.

2. Experimental setup

A standard wet etching process with hydrofluoric acid (HF) and an ammonia fluoride (NH_4F) buffer was used for cleaning on-oriented 4'' boron-doped Si(111) substrates [28]. The hydrogen terminated Si-wafers were loaded into an ultrahigh vacuum chamber (UHV) with a base pressure of 3×10^{-10} mbar. To achieve the (7×7) -Si(111) surface reconstruction, the samples were annealed at 750 °C for 5 minutes. Afterwards the substrate temperature was reduced to 625°C for the oxide deposition by molecular beam epitaxy (MBE). The shutter to the praseodymium oxide target was opened first for 20s to get an ultra-thin buffer layer, to avoid reactions between CeO_2 and Si [39]. Then, the cerium oxide source was additionally opened for co-evaporation. The different stoichiometries were achieved by varying the power of the respective electron evaporators. The total deposition rate of cerium and praseodymium oxide was kept at about 6 nm/min to a total thickness between 8-22nm. During oxide deposition, the chamber pressure raised typically up to 3×10^{-6} mbar.

X-ray photoemission spectroscopy (XPS) was used with MgK_{α} excitation energy ($E_{\text{exc}}=1253.6\text{eV}$) and a *Phoibos HSA 3500* analyser from *SPECS* in constant pass energy mode to determine the $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0-1$) stoichiometries. The crystal structure was

characterized in terms of layer orientation and strain status by X-ray diffraction (XRD) with a *DMAX 1500* and a *SmartLab* from *Rigaku* (CuK $_{\alpha}$ -radiation ($\lambda=0.154$ nm)). Synchrotron radiation-grazing incidence X-ray diffraction (SR-GIXRD) was performed at beam line W 1 of the Deutsches Elektronen Synchrotron (DESY) ($E=10.5$ keV) to investigate twin formation and identify the phases with high sensitivity and resolution. Bragg peaks are always indexed with respect to bulk coordinates.

3. Results & Discussion

3.1 XPS

For the stoichiometry determination of the three Ce $_{1-x}$ Pr $_x$ O $_{2-\delta}$ ($x = 0-1$) thin films, we recorded Ce3d and Pr3d core level XPS spectra in the binding energy (BE) region from 984eV to 876eV. For all spectra shown in figures 1a-d, we subtracted a Shirley background.

In particular, in Fig. 1a we compared all samples of different stoichiometry in one graph with the contributions from Pr and Ce for each sample. We normalized the XPS spectra intensity to the Pr contributions making it possible to deduce the stoichiometry directly from the Ce peak intensities in Fig. 1a. In detail, the stoichiometries were analysed as described by Briggs and Seah [40]. The relation of the 3d peak areas $I^{\text{Pr}3d}/I^{\text{Ce}3d}$ were calculated taking into account the cross sections σ ($\sigma^{\text{Pr}3d}/\sigma^{\text{C}1s} = 51.9$, $\sigma^{\text{Ce}3d}/\sigma^{\text{C}1s} = 48.2$) calculated by Scofield [41], the transmission efficiency $T(E_{\text{kin}})$ of the spectrometer ($E_{\text{kin}}^{\text{Pr}3d} = 314$ eV, $E_{\text{kin}}^{\text{Ce}3d} = 362$ eV), and the inelastic mean free paths λ ($\lambda^{\text{Pr}3d} = 8.42$ Å, $\lambda^{\text{Ce}3d} = 9.18$ Å) calculated by the TPP-2M formula [42]. We assumed that the inelastic mean free paths do not change with stoichiometry, due to the fact that they are almost identical for pure Pr $_2$ O $_3$ and CeO $_2$. The difference in the angular asymmetry function L for Ce3d and Pr3d is also insignificant. Furthermore, in constant pass energy mode, variations in the analysed area and detector efficiency were negligible. It turned out that the three Ce $_{1-x}$ Pr $_x$ O $_{2-\delta}$ /Si(111) samples contain low ($x = 0.3$), medium ($x = 0.7$) and high ($x = 0.8$) Pr concentrations. We estimate the error

bars (background differences, matrix effects etc.) in determining the stoichiometry by about $\Delta x = \pm 0.05$. The Pr related regions split into two parts, due to a spin-orbit coupling ($\text{BE}(\text{Pr}3d_{3/2}) - \text{BE}(\text{Pr}3d_{5/2}) \sim 20\text{eV}$). The signals can be clearly assigned to the Pr^{3+} initial state, due to the XRD Pr_2O_3 structure results (see below). In addition, final state effects occur, which are indicated in Fig. 1a by the $\text{Pr}3d$ peak labels. Namely, after the emission of the $\text{Pr}3d$ photoelectron from the $3d^{10}4f^2$ electron configuration a core hole ($\underline{c}$) is left behind and a further charge transfer from the $\text{O}2p$ to an empty $\text{Pr}4f$ state creates a valence band hole ($\underline{v}$) resulting in the final states $4f^2\underline{c}$ and $4f^3\underline{cv}$, respectively [43,44].

In contrast to the Pr contribution, Ce valence states can be rather easily detected by different peak shapes. Therefore, we consider the $\text{Ce}3d$ BE region from 922 eV to 876 eV in more detail to analyse the corresponding stoichiometries (Figs. 1b-d). All peak line shapes were fitted by Voigt functions. The XPS spectra of the Ce regions also show a spin-orbit coupling ($\text{BE}(\text{Ce}3d_{3/2}) - \text{BE}(\text{Ce}3d_{5/2}) \sim 18\text{eV}$). The deconvolution exhibit contributions from the Ce^{3+} and Ce^{4+} initial states, which have the $3d^{10}4f^1$ and $3d^{10}4f^0$ electron configurations, respectively. Furthermore, for Ce^{3+} two final states ($4f^1\underline{c}$ and $4f^2\underline{cv}$) and for Ce^{4+} three final states ($4f^0\underline{c}$, $4f^1\underline{cv}$ and $4f^2\underline{cv}^2$) exist after photoemission and $\text{O}2p\text{-Ce}4f$ hybridization. A multitude of 10 peaks is resulting, which we designated (Tab. 1) according to literature [45-47].

In the following, we will discuss the correlation between $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ stoichiometries and the Ce valence states in a qualitative way. It is obvious that the $\text{Ce}^{3+}/\text{Ce}^{4+}$ ratio is increasing with increasing Pr^{3+} doping (Figs. 1b-d). While for $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$ (Fig. 1b) and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$ (Fig. 1c) the Ce^{4+} concentration is dominant, no Ce^{4+} ions can be observed in the $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}/\text{Si}(111)$ (Fig. 1d) sample. It should be pointed out that satellite signals (S_1 and S_2) were observed in the spectra, whose origin is still under debate in literature [48].

After analysing the stoichiometries and valence states by XPS, we performed an extensive XRD study for correlation with the crystal structure of the $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}/\text{Si}(111)$ samples.

3.2 XRD

Vertical epitaxial relationships: We characterized the vertical epitaxial relationships for first information about the crystal phase of the $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$, $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$ and $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}/\text{Si}(111)$ heterostructures in the following by specular θ - 2θ scans from 55° to 65° (Figs. 2a-c). In Fig. 2 the theoretical Bragg peak positions (dotted lines) of the pure bulk oxide planes (cub- $\text{Pr}_2\text{O}_3(444)$ $2\theta = 57.18^\circ$; $\text{CeO}_2(222)$ $2\theta = 59.09^\circ$; hex- $\text{Pr}_2\text{O}_3(0004)$ $2\theta = 61.66^\circ$) are compared with the experimental mixed oxide peaks. In all graphs, the sharp double peak with highest intensity can be assigned to $K_{\alpha 1}$ and $K_{\alpha 2}$ (222) reflections of the Si(111) wafers ($2\theta = 58.88^\circ$). Fig. 2a shows the specular θ - 2θ scan of the $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$ sample. The experimental Bragg peak ($2\theta = 58.68^\circ$, $d = 1.571 \text{ \AA}$) is shifted toward the lower angle side of the bulk $\text{CeO}_2(222)$ reflection ($2\theta = 59.09^\circ$, $1.562 \text{ \AA}$). This trend is enhanced for the more Pr containing $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$ heterostructure (Fig. 2b), namely the Bragg peak is shifted further to lower angles ($2\theta = 58.00^\circ$, $d = 1.588 \text{ \AA}$) closer to the bulk cub- $\text{Pr}_2\text{O}_3(444)$ reflection ($2\theta = 57.18^\circ$, $d = 1.609$). We can thus tentatively assign the observed Bragg peaks of $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}$ and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}$ to cubic related fluorite lattices in (111) orientation whose lattice constant is increased by Pr^{3+} incorporation. In contrast, the $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}/\text{Si}(111)$ Bragg reflection ($2\theta = 60.80^\circ$, $d = 1.522 \text{ \AA}$) in Fig. 2c is situated at the higher angle side close to the bulk peak position of pure hex- $\text{Pr}_2\text{O}_3(0004)$ ($2\theta = 61.66^\circ$, $d = 1.502 \text{ \AA}$), indicating a hexagonal (0001) oriented $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}$ mixed oxide lattice.

Lateral epitaxial relationships: We applied [10L] and [-10L] rod scans by SR-GIXRD for the cubic mixed oxide samples $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}(111)/\text{Si}(111)$ and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}(111)/\text{Si}(111)$ (Figs. 3a-d) to study the lateral epitaxial relationship. Additionally, we can identify so-called stacking twins of type-A and type-B orientation, which exhibit an ABCABC... (defined as stacking sequence of the Si substrate) and BACBAC... stacking sequence, respectively [49].

In other words, type-A and type-B domains belong to the class of rotation twins, which are related to each other by a 180° rotation around the (111) axis.

In the scans along the [10L] rod of the samples $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$ (Fig. 3a) and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$ (Fig. 3b), we identified the sharp and highly intense $\text{Si}(11-1)$ ($L = 1/3$ *r.l.u.*) and $\text{Si}(220)$ ($L = 4/3$ *r.l.u.*) Bragg peaks. Due to the limited film thickness, the mixed oxide (002) and (113) reflections are broader and localized at about $L = 2/3$ *r.l.u.* and $L = 5/3$ *r.l.u.*, correspondingly. This indicates that the mixed oxides are type-B oriented. Similar type-B oriented $\text{CeO}_2(111)$, $\text{PrO}_2(111)$ and $\text{Pr}_2\text{O}_3(111)$ thin films on a $\text{Si}(111)$ substrate were already observed in literature [14,29,30,32,39]. However, to find potential stacking twins of type-A orientation, we also scanned along the [-10L] rods (Figs. 3c, d). Here, we can find the type-B related mixed oxide (1-11) and (202) peaks close to $L = 1/3$ *r.l.u.* and $L = 4/3$ *r.l.u.*, respectively. Furthermore, we localized the $\text{Si}(131)$ reflection at $L = 5/3$ *r.l.u.*, but the $\text{Si}(020)$ at $L = 2/3$ *r.l.u.* is kinematically forbidden. The absence of the $\text{Si}(020)$ Bragg peak offers the opportunity to investigate potential type-A oriented mixed oxide stacking twins at this position. Indeed, we observe weak signals at the position $L = 2/3$ *r.l.u.* for $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}(111)/\text{Si}(111)$ and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}(111)/\text{Si}(111)$, which we can assign to the type-A mixed oxide (020) reflection. Comparing the intensities of the type-B (002) reflections (I_B) with the type-A (020) reflections (I_A), we can roughly estimate the population ratio of stacking twins. In this way, we determined that the $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}(111)/\text{Si}(111)$ and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}(111)/\text{Si}(111)$ samples contain less than 0.1% and 1% type-A oriented domains, respectively. Therefore, the main lateral epitaxial relationships of the oxide heterostructures are given by $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}\langle 1-10 \rangle \parallel \text{Si}\langle -110 \rangle$ and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}\langle 1-10 \rangle \parallel \text{Si}\langle -110 \rangle$.

To determine the lateral epitaxial relationship of the hexagonal $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}(0001)/\text{Si}(111)$ sample, we applied a laboratory based pole figure measurement (Fig. 4). To simultaneously get information about the orientation of the Si substrate and the mixed oxide thin film, we chose a 2θ angle of 56.5° . This position is situated between the $\text{Si}\{113\}$ (open triangles: $\chi =$

29.50°), Si{1-13} (open squares: $\chi = 58.52^\circ$), Si{-1-13} (open pentagons: $\chi = 79.98^\circ$) related Bragg peaks ($2\theta = 56.13^\circ$) and the pure hex- $\text{Pr}_2\text{O}_3\{02-21\}$ (open circles: $\chi = 75.00^\circ$) related Bragg peaks ($2\theta = 57.19^\circ$). The pole figure study allows thus by the detection of the 6-fold symmetry of the hexagonal $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}(0001)$ thin film and the Si substrate Bragg peaks to determine the lateral epitaxial relationship, namely $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}\langle 11-20 \rangle \parallel \text{Si}\langle -110 \rangle$.

To summarize the epitaxial relationship XRD study, these results imply that the samples with low ($x = 0.3$) and medium ($x = 0.7$) Pr^{3+} concentration are cubic based (111) oriented structures. However, it is not yet clear whether the cubic phases are bixbyite and/or fluorite related. In contrast, the specular θ - 2θ and pole figure scan of the sample with high ($x = 0.8$) Pr^{3+} concentration clearly identified a hexagonal (0001) oriented lattice. We will clarify the phase of the cubic mixed oxide heterostructures by additional synchrotron and laboratory based in-plane XRD measurements.

Crystal phase: To clarify to which extend the mixed oxides $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$ and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$ exhibit a fluorite (f) or bixbyite (bb) lattice we applied an in-plane analyses of the cubic mixed oxide samples $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$ and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$ by SR-GIXRD measurements along the [H00] direction (Figs. 5a, b). We expect the bb(33-6) reflection at about $H = 2.25$ assuming that the bulk lattice constant is about twice as big as the fluorite related lattice constant. In Fig. 5a we can only observe a single peak close to the position $H = 3$, which can be attributed to the f(22-4) Bragg reflection. The fluorite related (11-2) reflection cannot be observed, due to a very small structure factor. In contrast, Fig. 5b reveals the bb(33-6) reflection at about $H = 2.25$. Therefore, the Bragg reflection close to the position $H = 3$ is not only attributed to the (22-4) peak of the fluorite lattice, but also to the bixbyite (44-8) reflection. It is noted that the peak is not exactly situated at the position $H = 3$, which indicates that the film is not pseudomorphic. The additional very sharp signals at $H = 1$ can be assigned to the Si crystal truncation rods (CTR). Further oxide peaks cannot be observed, because the bb(22-4) and f(11-2) reflection have too small structure factors and the

bb(11-2) is probably overshadowed by the diffuse x-ray scattering background. Concluding, we found that the $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}$ mixed oxide is grown only in a fluorite structure. However, the $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}$ mixed oxide exhibits a bixbyite and fluorite phase.

Strain status: We applied additional θ - 2θ XRD scans to determine the strain status of both cubic mixed oxide thin films by the $\cos^2\chi_{(hkl)}$ method (Figs. 5c, d) [50]. Therefore, we determined the θ value of several Bragg reflections with different inclinations $\chi_{(hkl)}$ with respect to the Si(111) surface normal. Afterwards, we calculated the lattice plane distances $d_{(hkl)}$ and the corresponding cubic lattice constants $a_{(hkl)}$ under the assumption of an unstrained film. Since the assumed lattice constant $a_{(hkl)}$ is linearly proportional to $\cos^2\chi_{(hkl)}$, this method allows to determine the in-plane lattice constant a_0 and off-plane lattice constant a_l by approximating to $\cos^2\chi_{(hkl)} = 0$ ($\chi_{(hkl)} = 90^\circ$) and $\cos^2\chi_{(hkl)} = 1$ ($\chi_{(hkl)} = 0^\circ$), respectively. Fig. 5c ($\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$) and Fig. 5d ($\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$) show the $\cos^2\chi_{(hkl)}$ plots for various Bragg reflections ($\chi_{(11-1)} = 70.5^\circ$, $\chi_{(400)} = 54.7^\circ$, $\chi_{(3-13)} = 48.5^\circ$, $\chi_{(220)} = 35.3^\circ$, $\chi_{(311)} = 29.5^\circ$, $\chi_{(422)} = 19.5^\circ$ and $\chi_{(222)} = 0^\circ$). The approximated in-plane lattice constants are $a_0 = 5.45 \text{ \AA}$ and $a_0 = 5.51 \text{ \AA}$ for $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}(111)/\text{Si}(111)$ and $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}(111)/\text{Si}(111)$, respectively. The linear regressions of this peak positions show only very small slopes, which means that the films of the cubic mixed oxide phases are almost unstrained and in- and off-plane lattice constants are almost identical. Furthermore, these values are not matching to the Si(111) in-plane constant $a_0 = 5.43 \text{ \AA}$. These results thus reveal fully relaxed cubic mixed oxide thin films. As consequence, we can state that the observed peak shift in the specular θ - 2θ scans is not extrinsically caused by lattice mismatch strain between the oxide film and Si(111) but intrinsically by Pr^{3+} doping, which increases the lattice constants due to the bigger ionic radius of Pr^{3+} ($1.266 \text{ \AA}$) in respect to Ce^{4+} ($1.110 \text{ \AA}$) [51]. Furthermore, this enables a comparison of the lattice constants from the mixed oxides with the bixbyite related (cub- $\text{Pr}_2\text{O}_3^{\text{bulk}}$) or fluorite related ($\text{CeO}_2^{\text{bulk}}$) pure oxides. In particular, the lattice constant of $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$ (Fig. 5c: $a = 5.45 \text{ nm}$) is closer to the fluorite related lattice of $\text{CeO}_2^{\text{bulk}}$

($a = 5.41$ nm). We thus conclude that the $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}$ oxide film is characterized by a fluorite phase whose lattice constant is increased by Pr^{3+} doping. However, the lattice constant of $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$ (Fig. 5d: $a = 5.51$ nm) is closer to the bixbyite related lattice constant of $\text{cub-Pr}_2\text{O}_3^{\text{bulk}}$ ($a/2 = 5.58$ nm). This points to a bixbyite $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}$ matrix whose lattice constant is decreased by fluorite related inclusions.

4. Summary & Outlook

In conclusion, single crystalline $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0-1$) mixed oxide thin films with three different stoichiometries were grown on a Si(111) substrate by co-evaporating MBE. Laboratory- and synchrotron-based XRD was applied to determine the crystal phases and proved the formation of homogeneous single crystalline $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0-1$) mixed oxide films so that surface sensitive XPS studies could be applied for stoichiometry determination. A consistent structure-stoichiometry picture resulted from the combined XPS-XRD study and the main epitaxial relationships are the following:

$\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}(111); \langle 1-10 \rangle / \text{Si}(111); \langle -110 \rangle$

$\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}(111); \langle 1-10 \rangle / \text{Si}(111); \langle -110 \rangle$

$\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}(0001); \langle 11-20 \rangle / \text{Si}(111); \langle -110 \rangle$

In particular, according to XRD and XPS $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$ exhibits a CeO_2 fluorite lattice with Pr^{3+} ions in substitutional sites causing an extension of the lattice constant and a related oxygen deficiency. In $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$, XRD and XPS detected a further extended lattice constant and increased amount of Ce^{3+} ion. The rare earth ion concentration with a 3+ valence state is dominating, indicating a bixbyite matrix. The Ce^{4+} contribution is pointing to an additional fluorite phase. We propose, in agreement with literature [38], a bixbyite matrix with coexisting fluorite inclusions. In contrast to the above mentioned mixed oxide heterostructures, $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}$ films on Si(111) have a hexagonal lattice with Ce^{3+} ions in

substitutional sites. It is noted that the existence of such a phase was not reported by bulk powder studies.

In view of future model catalyst experiments, we will investigate the implication of structural differences and Ce^{3+} stabilization to oxidation and reduction processes on mixed, single crystalline $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}$ ($x = 0-1$) films. In particular, adsorption and catalytic reaction of methanol at the mixed oxide surfaces will be of interest to evaluate the potential of tailored catalyst properties.

g) Acknowledgements

Portions of this research were carried out at the light source W1 at DESY. DESY is a member of the Helmholtz Association (HGF). We would like to thank W. Caliebe for assistance. Furthermore, we are grateful to the “Deutsche Forschungsgemeinschaft” (DFG) for financial support.

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j) Tables

Ion	Designation (Ce3d _{3/2} / Ce3d _{5/2})	Initial state	Final state
Ce ³⁺	v ₀ / u ₀	3d ¹⁰ 4f ¹	3d ⁹ 4f ² <u>cv</u>
	v' / u'	3d ¹⁰ 4f ¹	3d ⁹ 4f ¹ <u>c</u>
Ce ⁴⁺	v / u	3d ¹⁰ 4f ⁰	3d ⁹ 4f ² <u>cv</u> ²
	v'' / u''	3d ¹⁰ 4f ⁰	3d ⁹ 4f ¹ <u>cv</u>
	v''' / u'''	3d ¹⁰ 4f ⁰	3d ⁹ 4f ⁰ <u>c</u>

Table 1: Nomenclature used for the deconvoluted Ce3d XPS spectra in Fig. 1.

j) Figures

Figure 1: XPS 3d spectra of (a) all $\text{Ce}_{1-x}\text{Pr}_x\text{O}_{2-\delta}/\text{Si}(111)$ ($x = 0-1$) samples with different stoichiometry normalized to Pr intensity and subtracted Shirley background, (b) $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-\delta}/\text{Si}(111)$, (c) $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-\delta}/\text{Si}(111)$, and (d) $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-\delta}/\text{Si}(111)$.

Figure 2: Specular θ - 2θ XRD of (a) $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2-6}/\text{Si}(111)$, (b) $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2-6}/\text{Si}(111)$, and (c) $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2-6}/\text{Si}(111)$.

Figure 3: SR-GIXRD scan along [10L] rod of (a) Ce_{0.7}Pr_{0.3}O_{2-δ}/Si(111), (b) Ce_{0.3}Pr_{0.7}O_{2-δ}/Si(111) and [-10L] rod of (c) Ce_{0.7}Pr_{0.3}O_{2-δ}/Si(111), and (d) Ce_{0.3}Pr_{0.7}O_{2-δ}/Si(111).

Figure 4: Pole figure of $\text{Ce}_{0.2}\text{Pr}_{0.8}\text{O}_{2.6}/\text{Si}(111)$ measured at $2\theta = 56.5^\circ$.

Figure 5: SR-GIXRD scan along [H00] direction of (a) $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2.6}/\text{Si}(111)$, (b) $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2.6}/\text{Si}(111)$ and strain measurement using $\cos^2\chi_{(hkl)}$ plot of (c) $\text{Ce}_{0.7}\text{Pr}_{0.3}\text{O}_{2.6}/\text{Si}(111)$, (d) $\text{Ce}_{0.3}\text{Pr}_{0.7}\text{O}_{2.6}/\text{Si}(111)$.