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SPECIAL TOPICS

Postdeposition annealing induced transition from hexagonal Pr_2O_3 to cubic PrO_2 films on Si(111)

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Films of hexagonal praseodymium sesquioxide ($h\text{-Pr}_2\text{O}_3$) were deposited on Si(111) by molecular beam epitaxy and thereafter annealed in 1 atm oxygen at different temperatures, ranging from 100 to 700 °C. The films of the samples annealed at 300 °C or more were transformed to PrO_2 with B -oriented $Fm\bar{3}m$ structure, while films annealed at lower temperatures kept the hexagonal structure. The films are composed of PrO_2 and $\text{PrO}_{2-\delta}$ species, which coexist laterally and are tetragonally distorted due to the interaction at the interface between oxide film and Si substrate. Compared to PrO_2 , $\text{PrO}_{2-\delta}$ has the same cubic structure but with oxygen vacancies. The oxygen vacancies are partly ordered and increase the vertical lattice constant of the film, whereas the lateral lattice constant is almost identical for both species and on all samples. The latter lattice constant matches the lattice constant of the originally crystallized hexagonal praseodymium sesquioxide. That means that no long range reordering of the praseodymium atoms takes place during the phase transformation. © 2009 American Institute of Physics. [DOI: 10.1063/1.3152796]

I. INTRODUCTION

Rare earth oxides have been investigated in the context of electro-optics,¹ sensor technology,² and catalytic reactions.³ They are also of special interest in microelectronics,⁴ where heteroepitaxial rare earth oxide films on Si have been studied intensively. One goal is to improve the performance of future Si device technologies by using epitaxial rare earth oxides on Si. Rare earth oxides have been discussed as single crystalline oxide films on Si systems, which, for instance, are studied as highly functional buffer oxide structures to achieve global integration of alternative semiconductors on Si. These engineered Si wafers have been developed with praseodymium oxide buffers among others, e.g., to integrate Ge on the platform of Si technology (GeOI).⁵ For all these applications, it is important to investigate the dependence of the oxide film structure and morphology on the preparation conditions to improve oxide film quality.

Single crystalline rare earth oxide films on Si are also of interest in the field of model catalysis studies to investigate catalytic reactions on the atomic scale.⁶ For instance, praseodymia serves as catalyst for the oxidative coupling of methane.^{8,9} The high mobility of lattice oxygen is accompanied by oxidation or reduction in praseodymium oxide and leads to different valences of the Pr ions. This effect is accompanied by the generation of oxygen vacancies so that praseodymium oxides form a complicated phase diagram.¹⁰ Thin lanthanide oxide films on Si form interfacial silicate layers when they are annealed to several hundred degree Celsius.⁷ The ion radius of lanthanides decreases with increasing atomic number. This effect is also known as lan-

thanide contraction. Ono and Katsumata⁷ observed that the thickness of the interfacial layer decreases significantly with higher atomic numbers and attribute this to the decrease in the ion radius. Therefore, the interfacial layer formed during the annealing process is most pronounced for praseodymium oxide because of its large ion radius compared to the radii of other lanthanides.

Crystalline hexagonal $h\text{-Pr}_2\text{O}_3(0001)$ films can be formed on clean Si(111) surfaces by molecular beam epitaxy (MBE).¹¹ The lateral lattice mismatch of these two materials is only 0.5%, while the vertical lattice mismatch is 4.2%. The hexagonal structure of praseodymium oxide, however, is unstable if exposed to air at room temperature and tends to form hydroxides.

If $h\text{-Pr}_2\text{O}_3(0001)$ films are annealed in 1 bar nitrogen¹¹ or 10^{-5} mbar oxygen¹² atmosphere, an interfacial layer is formed and the films are transformed to cubic $c\text{-Pr}_2\text{O}_3$ (bixbyite structure with $Ia\bar{3}$ symmetry),¹² which is stable under normal temperature and pressure. The lattice constant of bulk $c\text{-Pr}_2\text{O}_3$ is approximately twice as large as the lattice constant of Si. A residual lattice mismatch of 2.7% is obtained if one compares the lattice constant of $c\text{-Pr}_2\text{O}_3$ with the doubled lattice constant of Si. Therefore, $c\text{-Pr}_2\text{O}_3$ films form antiphase domains on Si(111) substrates since $c\text{-Pr}_2\text{O}_3$ can nucleate on different sublattices on Si(111). For buffer layers, however, antiphase boundaries are disadvantageous if heteroepitaxial films are deposited.^{13–15} Therefore, PrO_2 (fluorite structure with $Fm\bar{3}m$ symmetry) has the big advantage that its lattice constant matches almost exactly the lattice constant of Si. The residual lattice mismatch is only -0.7% . PrO_2 films on Si(111) are obtained if $h\text{-Pr}_2\text{O}_3$ films are annealed in 1 bar oxygen atmosphere, as we reported previously.¹⁶ Here we will show that these films can be pre-

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pared by annealing at different temperatures between 300 and 700 °C and that these films consist of two laterally coexisting praseodymia species, namely, PrO_2 and under stoichiometric $\text{PrO}_{2-\delta}$. We will also investigate the influence of the annealing temperature on the interface between oxide and substrate and on the homogeneity of the oxide film.

II. EXPERIMENTAL

Boron doped Si(111) wafers ($\rho=5\text{--}15\ \Omega\text{ cm}$ and orientation $=0.35 \pm 0.15^\circ$) were cleaned by the standard “piranha etch” procedure.¹⁷ The samples were subsequently etched in 40% NH_4F solution for 30 min and rinsed in deionized water for 5 min to prepare atomically smooth surfaces.^{18–20} Afterward, they were introduced into an UHV chamber with base pressure in the 10^{-10} mbar range. The H-terminated Si wafers were then heated at 700 °C for 5 min to prepare clean surfaces with (7×7) superstructures.

Ultrathin $h\text{-Pr}_2\text{O}_3$ films of 5 nm thickness were deposited on the wafers via MBE at a rate of 0.1 nm/s using highly purified Pr_6O_{11} , which was reduced to Pr_2O_3 before the evaporation process. The substrate was heated to 625 °C and the pressure was in the 10^{-8} mbar range during evaporation.

Thereafter, the samples were removed from the chamber and annealed in 1 atm oxygen for 30 min to obtain PrO_2 with cubic fluorite structure. Different temperatures between 100 and 700 °C were used during this postdeposition annealing (PDA) process.

X-ray photoelectron spectroscopy (XPS) was performed in a Perkin Elmer PHI 5600 ci ESCA apparatus with monochromatic $\text{Al } K_\alpha$ radiation ($\hbar\omega=1486.6\text{ eV}$) and a hemispherical mirror analyzer with an energy resolution smaller than 0.4 eV. For sputter experiments, the samples were bombarded by Ar^+ ions (Ar pressure of 10^{-7} mbar). The incidence angle was 60° and the energy of the ions was 1.5 keV.

X-ray reflection (XRR) and x-ray diffraction (XRD) measurements in θ - 2θ geometry were carried out at beamline W1/HASYLAB using a six circle diffractometer and a beam energy of 10.0–10.5 keV. Grazing incidence XRD (GIXRD) was performed at beamline BW2/HASYLAB using a beam energy of 10.0 keV and incidence angles from 0.4° to 0.8° . This is higher than the critical angles for both silicon (0.18°) and praseodymium oxides of different stoichiometry (0.28°).^{21,22} Therefore, the estimated penetration depth is 1850–3700 nm for Si and 55–110 nm for praseodymium oxides in our GIXRD studies. During XRD measurements, higher angles than 0.8° were used, resulting in even higher penetration depths than calculated for our GIXRD measurements. Because of that, a strong Si signal is visible in all of the presented XRD and GIXRD measurements and can be used for calibration. As the Si unit cell in real space and thus also the reciprocal unit cell of the underlying Si crystal are very well known, this increases the accuracy of our measurements significantly.

III. RESULTS

A. Sputter XPS

Figure 1 shows the results of sputter XPS measurements of the Pr 3d region of a sample that was annealed in 1 bar

FIG. 1. Sputter XPS measurement of the Pr 3d region of a 5 nm praseodymium oxide on Si(111) sample after PDA at 450 °C in 1 bar oxygen. After 3 min of sputtering (top line), an intensity peak is visible at 967 eV. This $\text{Pr } 3d_{3/2}4f^1$ peak, which is characteristic of stoichiometric PrO_2 , disappears during the sputter process, although there is still praseodymium on the sample, as verified by the residual $\text{Pr } 3d_{3/2}$ and $\text{Pr } 3d_{5/2}$ peaks. This effect is related to preferential sputtering of oxygen and thus reduction in the oxide.

oxygen at 450 °C for 30 min to obtain PrO_2 . The top line was measured after a $t_{\text{sp}}=3$ min sputter cycle to clean the surface. The following lines were recorded after additional sputter cycles of $\Delta t_{\text{sp}}=15$ min each.

Our results for Pr 3d electrons can be compared to XPS measurements by Lütkehoff *et al.*²³ on bulk praseodymium oxide. For praseodymium oxides of different stoichiometry, $3d_{5/2}$ and $3d_{3/2}$ peaks can be expected at 935 and 955 eV, respectively.²⁴ These peaks split into additional satellite features due to final state and multiplet effects.²⁵ The most prominent one can be seen at 931 eV and a clean and sharp satellite peak should build up for single crystalline and stoichiometric PrO_2 . Our XPS results agree well with the bulk results. However, these photoelectron peaks cannot be used to distinguish between different stoichiometries. According to Lütkehoff *et al.*,²³ an O-KLL Auger peak is visible at 972 eV as well as an additional $\text{Pr } 3d_{3/2}4f^1$ peak at 967 eV, which appears only for PrO_2 but not for praseodymia with less oxygen. As this peak appears in our measurements first and then disappears during the sputter process, we can conclude that the oxide film exhibits partly or completely PrO_2 stoichiometry. The intensity of the main Pr 3d peaks and of the O-KLL Auger peak, however, does not disappear as fast as the intensity of the named PrO_2 specific $\text{Pr } 3d_{3/2}4f^1$ peak at 967 eV. Therefore, the stoichiometry of the oxide changes during the sputter process. XRD measurements, which we discuss later in this article, show that without sputtering, the film has a continuous stoichiometry. That means that the reduction in the oxygen during the sputter XPS measurements must be attributed to preferential sputtering of oxygen. The Pr 3d and O 1s signals do *not* disappear completely during the sputter

FIG. 2. (Color online) Sputter XPS measurement of the Si 2p region of a 5 nm praseodymium oxide on Si(111) sample after PDA at 450 °C in 1 bar oxygen. The top line was measured after 3 min of sputtering to clean the surface. After 33 min of sputtering, silicate and Si are detected. After further sputtering, the silicate signal disappears and the signal of bulk Si remains.

process due to intermixing effects between film and substrate as reported before in Ref. 26.

Figure 2 presents complementary results for Si 2p photoelectrons. No Si signal is visible after 3 and 18 min of sputtering. After 33 min, Si is detected at a binding energy of 99.3 eV. Another peak appears at a binding energy of 102.6 eV, which is close to the binding energy of 103.3 eV reported for SiO₂.²⁷ Therefore, we attribute this peak to the formation of SiO₂-rich silicate at the interface between oxide film and Si(111) substrate. The large content of Si–O–Si bonds observed here agrees well with the results by Ono *et al.*⁷ In the following sputter cycles, the silicate peak disappears for $t_{sp} \geq 60$ min and only bulk Si remains.

The O 1s XPS signal of the same sample is presented in Fig. 3. The double peak structure visible at the beginning is due to stoichiometric PrO₂. For $t_{sp}=18$ min, the binding energy shifts from the PrO₂ state toward higher bindings during the sputter process, a process that was also reported by Giusani *et al.*⁵ during the reduction in oxide in a PrO₂ film via Ge deposition. This reconfirms the oxygen loss due to preferential sputtering of oxygen. After $t_{sp} \geq 50$ min, a single O 1s peak appears at 531.4 eV binding energy, which can be attributed to the formation of Pr-silicate at the interface between praseodymium oxide film and Si(111) substrate.

In summary, our sputter XPS results demonstrate that a very thin SiO₂-rich silicate is formed at the interface between oxide film and substrate as reported by Ono and Katsumata⁷ and that the PrO₂ film loses oxygen during the sputter process.

B. X-ray reflectometry

XRR measurements were performed on 5 nm praseodymium oxide samples that had been annealed at different temperatures for 30 min each, with temperatures ranging from

FIG. 3. Sputter XPS measurement of the O 1s region of a 5 nm praseodymium oxide on Si(111) sample after PDA at 450 °C in 1 bar oxygen. The double peak at the beginning of the sputter process is due to PrO₂. The relative intensities of the two peaks shift due to preferential sputtering of oxygen. The single peak after a sputter time of $t_{sp} \geq 45$ min is related to silicate.

$T_A=400$ °C to $T_A=700$ °C. Ono and Katsumata⁷ showed that in general lanthanide (Ln) oxides on Si form an interfacial layer during annealing processes that consists of two sublayers. One of those sublayers is Ln-rich and adjacent to the Ln-oxide, while the other one is SiO₂-rich and located between the Ln-rich layer and the Si substrate.

Our XRR measurements were fitted using the Parratt²⁸ algorithm and the model described above with an SiO₂-rich and a Pr-rich silicate interface layer. Thickness results of the Pr-rich interface film can be extracted from Fig. 4, which also shows a comparison of experimental data and fitted XRR curves. A reliable determination of the thickness of the SiO₂-rich silicate interface layer was not possible, as SiO₂-rich silicate and Si (substrate) have similar electron densities so that the results scatter, whereas the densities of the Pr-rich interface layer and the oxide as well as Si differ significantly. Figure 4 shows that a significant Pr-rich interface layer has formed only after PDA at $T_A \geq 500$ °C. We see a strong growth of the interface layer thickness with higher temperatures.

An additional sample was prepared under identical terms and postdeposition annealed at 800 °C (not shown here). As XRD measurements could not detect a crystalline oxide layer and praseodymium oxide does only evaporate at much higher temperatures, we assume that the whole 5 nm oxide layer has been transformed to an amorphous Pr–O–Si layer of more than 5 nm thickness in this case. This supports the results presented above that the formation of Pr-rich silicate at the interface between PrO₂ film and Si substrate is strongly enhanced for $T_A \geq 500$ °C.

Transmission electron microscope images in Ref. 12 show the segmentation of the interface into two sublayers with a well defined interface. XRR results with respect to

FIG. 4. (Color online) Top: experimental XRR data (dotted line) and simulated fitting curves (solid line) for three samples postdeposition annealed at different temperatures. Experimental and simulated data agree excellently. Bottom: thickness of the Pr-rich interface for different PDA temperatures. No Pr-rich layer is detected for temperatures below 500 °C. At higher temperatures, a Pr–O–Si layer is detected. Its thickness depends strongly on the PDA temperature.

stoichiometry and interface roughness are of high accuracy only for the samples annealed at 600 and 700 °C. For the samples annealed at lower temperatures, the accuracy is reduced because the condition (layer thickness) $\gg$ (interface roughness), which the Névo–Croce factor²⁹ (used here to describe the interface roughness) is based on, is not fulfilled. From the samples providing sufficient accuracy, the roughness between Pr-rich layer and SiO₂-rich layer is between 2 and 3 Å. The stoichiometry of the Pr-rich interface cannot be determined directly. Under the assumption that this layer is composed of Pr₂O₃ and SiO₂, as different crystalline silicates such as Pr₂SiO₅ and Pr₂Si₂O₇ are, the Pr-rich layer is composed of 30% SiO₂ and 70% Pr₂O₃ according to the electron density determined from the XRR analysis.

C. XRD and GIXRD

In the following, XRD and GIXRD measurements are presented. H , K , and L values of the indexed *peaks* are chosen with respect to the bulk lattices of the corresponding material and will be referred to as $(HKL)_B$, whereas labeling of the *axes* and *rods* corresponds to the hexagonal Si(111) lattice in surface coordinates $(HKL)_S$. A schematic drawing of the bulk Bragg peak positions of different praseodymia and of Si(111) is presented in Fig. 5.

FIG. 5. (Color online) Two-dimensional view of the reciprocal space of different bulk praseodymium oxide species and bulk Si, all with (111) orientation. The broad yellow lines describe the scans shown in the following pictures in (00L)_S, (01L)_S, and (0K0)_S orientations. The narrow black lines indicate Si CTRs. Kinematically forbidden peaks are ignored. The exception to this rule is Si, where the kinematically forbidden (002)_S peak is indicated by a smaller symbol than the nonforbidden Si peaks because the intensity of this peak is not completely erased due to the nonsymmetric electron distribution of the Si atoms.

Specular θ -2 θ XRD scans [(00L)_S rods] are shown in Fig. 6. The hexagonal praseodymium oxide layers of 5 nm thickness were annealed in 1 atm O₂ at different temperatures from 100 to 700 °C for 30 min. Sharp Bragg peaks of the Si(111) substrate can be found at $L=1$ and $L=3$. This corresponds to surface HKL values of Si(001)_S and Si(003)_S and bulk values of Si(111)_B and Si(333)_B. The kinematically forbidden Si(002)_S [Si(222)_B] peak can be found at $L=2$. It is allowed due to the nonisotropic electron density distribution of the Si atom but much weaker than Si peaks, which are not kinematically forbidden. Close to the Si peaks there are additional much broader Bragg peaks and fringes from the structure and film thickness, respectively, originating from the praseodymium oxide films.

The first Bragg peak at $L=1$ is difficult to analyze, as strong interference effects between Si substrate and oxide layer occur due to the amorphous interface layer between the two crystalline structures, which acts as a spacer. These interference effects are much weaker around the kinematically forbidden Si(222)_B peak due to the very weak diffraction of the Si substrate. This Si peak is strong enough to be used for calibration though, and it allows excellent analysis of the underlying PrO₂(222)_B peak due to its weak interference with the XRD signal from the oxide film.

FIG. 6. (Color online) $(00L)_S$ scans of several 5 nm praseodymia films on Si(111) samples after PDA in 1 bar oxygen for 30 min at different temperatures from 100 to 700 °C. Sharp Si peaks and broad underlying praseodymia peaks are visible at $L \approx 1$, $L \approx 2$, and $L \approx 3$ for $T_A \geq 300$ °C. For lower annealing temperatures the typical diffraction pattern of $h\text{-Pr}_2\text{O}_3$ is observed. Therefore, the phase transition from hexagonal to cubic praseodymium oxide happens between 200 and 300 °C.

It is obvious that the peak position of the oxide close to $L=2$ shifts considerably between 200 and 300 °C. Also, strong Bragg peaks at $L \approx 1.5$ and $L \approx 2.5$ are present for both the 100 and 200 °C samples but not for samples annealed at higher temperatures. These effects hint to a phase transformation from hexagonal Pr_2O_3 to cubic praseodymium oxide, as hexagonal praseodymium sesquioxide fulfills the Bragg condition under these scattering vectors as indicated in Fig. 5. Furthermore noteworthy is the fact that for *all* samples above 200 °C, the fringes around the $\text{PrO}_2(222)_B$ peak are stronger on the left side of the peak than on the right side. We will comment on this later.

$(01L)_S$ crystal truncation rods (CTRs) of several samples were obtained from GIXRD experiments and are presented in Fig. 7. Here, the phase transition from hexagonal to cubic unit cell between 200 and 300 °C is also clearly visible, as a hexagonal unit cell fulfills the Bragg condition at $L \approx 0.5$ and $L \approx 1.5$, whereas a *B*-oriented oxide film with both cubic structure and $(111)_{\text{film}} \parallel (111)_{\text{substrate}}$ fulfills the Bragg condition on $L \approx 0.33$ and $L \approx 1.33$ on the $(01L)_S$ rod (cf. Fig. 5). *A*-oriented $\text{PrO}_2(111)$ unit cells would fulfill Bragg conditions at $L \approx 0.67$ and $L \approx 1.67$ and can therefore be excluded. Figure 5 demonstrates that one cannot distinguish between $c\text{-Pr}_2\text{O}_3$ and PrO_2 from experiments on both the $(00L)_S$ and $(01L)_S$ CTRs. We therefore additionally performed in-plane $(0K0)_S$ scans, where the larger unit cell of $c\text{-Pr}_2\text{O}_3$ leads to additional Bragg peaks compared to PrO_2 and the two structures can thus be distinguished (cf. Fig. 5).

Figure 8 gives an overview of the $(0K0)_S$ -direction ($L=0.05$) in-plane scans of the 700 °C sample parallel to the surface as an example. The weak peaks at $K \approx 1$ and $K \approx 2$ are due to praseodymia CTRs. Because of the larger unit cell, a cubic Pr_2O_3 film would fulfill Bragg conditions at $K=1.46$ and $K=2.19$. This is obviously not the case here, and thus there is no cubic Pr_2O_3 on the sample. A broad praseodymium oxide Bragg peak can be found at $K=2.985$,

FIG. 7. (Color online) $(01L)_S$ CTR scans of several praseodymia films on Si(111) postdeposition annealed from 100 to 700 °C. All peaks and fringes are due to the praseodymia film. No *A*-type cubic praseodymium oxide, which would fulfill Bragg conditions at $L \approx 2/3$, is detected on the samples. The oxides on the 100 and 200 °C samples fulfill Bragg conditions at $L \approx 1/2$ and at $L \approx 1$ and are thus hexagonal. The remaining samples have *B*-type cubic structure, as the oxides on them fulfill Bragg conditions at $L \approx 1/3$ and at $L \approx 4/3$. The discussed Bragg peak positions are also presented graphically in Fig. 5.

slightly left from the sharp Si Bragg peak at $K=3$. The inset of Fig. 8 shows a close-up of the region around these two peaks of the 450, 550, and 700 °C samples. Striking is the almost exactly identical position of the oxide peaks of the different samples. Regardless of the large scattering vector ($K \approx 3$) and the accompanying high resolution, no splitting of the oxide Bragg peaks is observed. From the full width at half maximum we conclude a lateral grain size of 11 nm for the sample annealed at 450 °C and 15 nm for the 550 °C sample and for the 700 °C sample each.

The resulting lateral lattice constants of the three investigated samples are compared to the lateral lattice constants of bulk praseodymium oxide in Fig. 9. They are not only almost exactly the same for the different samples and different annealing temperatures, but they also match the lateral lattice constant of bulk $h\text{-Pr}_2\text{O}_3$, although there is no signifi-

FIG. 8. (Color online) In-plane $(0K0)_S$ scan of the sample annealed at 700 °C. Praseodymia CTRs are detected at $K \approx 1$ and $K \approx 2$, the $\text{Si}(2\bar{4}2)_B$ Bragg peak with a broad underlying praseodymia Bragg peak at $K=3$. Bragg peaks, which are related to $c\text{-Pr}_2\text{O}_3$ are not observed (cf. Fig. 5). The inset shows the region around $K=3$ for three different samples. The lattice constants of these samples in K -direction are extremely close to each other.

FIG. 9. (Color online) Lateral lattice constant determined for the praseodymia films from the data around $K=3$ in Fig. 8. The lattice constant matches almost exactly the lattice constant of bulk $h\text{-Pr}_2\text{O}_3(0001)$, although CTR measurements verified that no hexagonal structure is on the sample. The PrO_2 layers are therefore strained, and their horizontal lattice constants seem to be pinned to the value of bulk $h\text{-Pr}_2\text{O}_3$, which was originally grown on the sample and only later transformed to films with cubic structure.

cant amount of $h\text{-Pr}_2\text{O}_3$ on samples annealed at $T_A \geq 300^\circ\text{C}$, as was proved before by both (00L) and (01L) CTRs. In addition this result is also confirmed by the in-plane scans presented in Fig. 8 since $h\text{-Pr}_2\text{O}_3$ would have Bragg peaks at $K=0.995$ and $K=1.990$. This is not the case for the investigated samples with $T_A \geq 300^\circ\text{C}$.

These results mean that the praseodymium dioxide films annealed at $T_A \geq 300^\circ\text{C}$ are B -oriented and have $Fm\bar{3}m$ structure. The lattice constant in *lateral* direction is identical for all investigated samples regardless of the annealing temperature. In the following, we report on the analysis of the $\text{PrO}(222)_B$ peak to obtain more insight in the structure of the praseodymia film in *vertical* direction.

The analysis of the praseodymia peaks reveals that in all samples that were annealed at 300°C or higher, the peaks are composed of two subpeaks with vertical lattice constants close to each other. This is shown in example for three of these samples in Fig. 10, where two fitting functions were used for the diffraction from the oxide layer on each sample. The two functions are calculated from kinematic diffraction theory in order to determine the vertical layer distances, assuming that the (bulk) unit cell of the two oxide species is tetragonally distorted. This demonstrates that the oxide film consists of two oxide species with different layer spacings. We previously introduced that these species are stoichiometric PrO_2 and under stoichiometric $\text{PrO}_{2-\delta}$.¹⁶ The left subpeak is caused by the under stoichiometric $\text{PrO}_{2-\delta}$ part with oxygen vacancies, and the right subpeak is caused by the stoichiometric PrO_2 part.

Both contributions are added incoherently, representing two species of praseodymium oxide that coexist laterally. These two species will therefore be referred to as two columns; the model will be referred to as two column model. The resulting fit function for the diffracted intensity is of tremendously better agreement with the recorded data compared to a simpler model with only one oxide species. The model with two coexisting praseodymia species introduced in more detail in Ref. 16 is confirmed by a broader database

FIG. 10. (Color online) Top: close-up of three CTRs from Fig. 6. Data (black points) was fitted by a function (black line), which consists of two subfunctions originating from the two coexisting $\text{PrO}_{2-\delta}$ (green line) and PrO_2 (red line) praseodymia species. Both functions are calculated by kinematic diffraction theory. The PrO_2 peaks are located at higher scattering vectors and show weaker fringes compared to the $\text{PrO}_{2-\delta}$ peaks. This corresponds to a smaller vertical layer distance and higher roughness. The sharp and kinematically forbidden $\text{Si}(002)_s$ peak was removed for clearness. Bottom: vertical layer distances determined for the praseodymia films from the data around $L=2$ in Fig. 6. After the phase transition between 200 and 300°C , the peak can only be fitted using two coexisting praseodymia species as shown above. The points marked with a triangle have $h\text{-Pr}_2\text{O}_3$ stoichiometry, those with a square $\text{PrO}_{2-\delta}$ and those with a circle PrO_2 .

here for different samples annealed at different temperatures. $\text{PrO}_{2-\delta}$ has a bigger lattice constant compared to PrO_2 due to lower average ionization of the Pr atoms and thus larger ion radius, as proved for bulk praseodymia PrO_x of different stoichiometries and with increasing lattice constants from $x=2$ to $x=1.5$ due to periodically ordered oxygen vacancies.¹⁰

Figure 10 also gives an overview of the vertical layer distances determined from the Bragg peak at $L \approx 2$ for the praseodymium oxide layers. For comparison we also show the vertical layer distances of the bulk structures of $c\text{-Pr}_2\text{O}_3$ and PrO_2 as well as $\text{PrO}_{1.83}$. The latter two oxide stoichiometries are of interest since there is a miscibility gap between the two bulk species.¹⁰ Therefore, in addition, the expected layer distances of the different strained phases are shown assuming $\Delta d/d = \Delta a/a$ [Poisson ratio of $\nu=1/3$ (Refs. 16 and 30)] and using the lateral lattice constant, which has been determined from in-plane scans for the different oxide films (cf. Fig. 9)]. While we observe only one layer distance for the hexagonal Pr_2O_3 phase ($T_A \leq 200^\circ\text{C}$), the two column

model from Ref. 16 is necessary to obtain a decent fit for all samples annealed at more than 200 °C. The vertical lattice spacing of h -Pr₂O₃ is slightly expanded, as reported before for h -Pr₂O₃/Si(111) after annealing in low pressure oxygen.³¹ The variances from the bulk lattice constant of h -Pr₂O₃ may be due to both strain effects and/or oxygen vacancies, which lead to greater ion radii of praseodymium atoms and thus to larger unit cells. Therefore, we assume that either compressive strain from the underlying substrate occurs or the phase transition to the bigger c -Pr₂O₃ unit cell has already begun. A third possibility is that formation of Pr(OH)₃ hydroxides in the film has taken place and that this causes the slight expansion of the hexagonal unit cell.

Layer distances of the two oxide species with cubic symmetry vary significantly by several percent. The vertical lattice constants show a tendency to decrease with higher annealing temperatures. Because oxygen vacancies increase the lattice constants of praseodymia, this shows that samples annealed at higher temperatures tend to have fewer oxygen vacancies.

The splitting up of the praseodymium oxide peak, which we clearly observe on the (00L) rod is less visible for the (01L) rod. This is easily explained since the distance between peaks in reciprocal space is proportional to the scattering vector. For the (00L) rod we discussed the splitting for $L=2$, while on the (01L) rod we only measure Bragg peaks of the oxide film for $L \approx 1/3$ and $L \approx 4/3$. Thus the overlap between adjacent Bragg peaks of PrO₂ and PrO_{2-δ} is larger.

What strikes the eye in this context is the asymmetric distribution of the fringes around the oxide Bragg peaks. It is observed on the (00L)₅ rod for $L=2$ as well as on the (01L) rod for $L=4/3$, while it is less pronounced for $L=1/3$ on the (01L) rod. Thus the asymmetry is more noticeable at higher scattering vectors. In other words, it is more noticeable if the two subpeaks of the praseodymium oxide double peak are clearly separated. One explanation for these asymmetric fringes is that the fringes originate mainly from the left subpeak (lower L value), while the right subpeak has less fringes. The left subpeak is the PrO_{2-δ} peak and that means that the roughness of this column must be considerably smaller than that of the stoichiometric PrO₂ column. The fringes also get weaker as T_A increases, pointing to increasing roughness for samples annealed at higher temperatures.

Another possible explanation for the asymmetric fringe distribution is a beat of diffraction amplitudes from the two different columns. Our simulations (not shown here) show that in this case the damping of the fringes in principle occurs under different scattering vectors, depending on the difference of the two observed lattice constants. Because our samples have different lattice constants and the mentioned difference between the two lattice constants on a sample varies from 1.6% (600 °C sample) to 4.5% (300 °C sample), it is improbable that this effect causes weaker fringes on the *right* side of the Bragg peaks for all samples. Therefore, we assume that the aforementioned different roughnesses of the two columns are the reason for the asymmetric fringe distribution.

IV. DISCUSSION

Ono and Katsumata⁷ showed that the interfacial layer built up during annealing processes of lanthanide oxides consists of one SiO₂-rich silicate layer close to the Si substrate and one Ln-rich silicate interface layer close to the oxide film. The thickness of the SiO₂-rich sublayer depends on both the atmosphere and strongly on the temperature during the annealing process. As the results of Ono and Katsumata depend on transmission fourier transform infra red spectroscopy (FTIR), only trends for the number of Si–O–Si and Pr–O–Si bonds, respectively, could be quantified. Assuming that the SiO₂-rich layer has only few impurities and that almost all Si–O–Si bonds are located in the SiO₂-rich interface layer, Ono and Katsumata determined the thickness of the SiO₂-rich layer from the number of Si–O–Si bonds. This assumption, however, is not defensible for the Ln-rich silicate film as its exact stoichiometry is still unclear. Also, Ono and Katsumata did not present temperature dependencies of the number of Ln–O–Si bonds. However, they give a few data indicating that the thickness of the Ln-rich silicate interface layer depends strongly on both the lanthanide and the temperature during the annealing process. Complementary to Ono and Katsumata, we demonstrate from our results a very strong temperature dependency of the Pr-rich silicate layer thickness. This dependency is even stronger than the one for the SiO₂-rich part of the interface if we compare our data to the data of Ono and Katsumata. The nonexistence of the Pr-rich interface layer for annealing temperatures below 500 °C is verified by our sputter XPS data (see Fig. 2), where a SiO₂-rich silicate with almost no Pr–O–Si bonds is detected for the 450 °C sample. It has to be emphasized that the silicate only forms due to annealing in oxygen, while it is not observed for annealing under UHV conditions.¹¹

Via XRD and GIXRD measurements on different samples annealed from 100 to 700 °C, we observed that the phase transition from h -Pr₂O₃ to an $Fm\bar{3}m$ (fluorite) structure with B -orientation and coexisting PrO₂ and PrO_{2-δ} stoichiometries occurs for samples annealed at $T_A \geq 300$ °C for 30 min. This result agrees well with earlier work by Eyring and Baenziger,³² who studied the phase transition from h -Pr₂O₃ to PrO₂ for *bulk* praseodymia. They proposed a mechanism for the transition from the ACACAC stacking of the hexagonal phase to an ABCABC stacking of the cubic phase. The ACACAC stacking of h -Pr₂O₃ *films* on Si(111) has been confirmed from the structure analysis presented by Jeutter *et al.*³³ For praseodymia films on Si(111) with cubic symmetry, the substrate induces B -oriented PrO₂ films. Therefore, the stacking transition is from ACACAC to ACBACB (cf. Fig. 11).

The phase transition does not occur at samples annealed at $T_A \leq 200$ °C within 30 min. However, this does not necessarily mean that there is a certain temperature between 200 and 300 °C that must be exceeded during the annealing process to cause the phase transition. As Hyde *et al.*³⁴ and Burnham and Eyring³⁵ showed for bulk praseodymium oxide, the oxidation process depends on oxygen pressure, temperature, and time. The stoichiometry x of PrO _{x} *powders* can have different equilibrium values between 1.5 and 2.0, where x

FIG. 11. (Color online) Schematic drawing of the phase transition from $h\text{-Pr}_2\text{O}_3$ to PrO_2 . The stacking of the Pr and O crystal planes is signed by capital and low-case letters, respectively. Red and black arrows indicate the lateral movement of Pr and O ions, respectively. Blue arrows (labeled by +) show additional O crystal planes due to the oxidation of the $h\text{-Pr}_2\text{O}_3$ film. For the structural phase transition only small lateral shifts are necessary to change the stacking from ACACAC of $h\text{-Pr}_2\text{O}_3$ to the ACBACB stacking of B -oriented PrO_2 , while the stacking of the first $h\text{-Pr}_2\text{O}_3$ layer at the interface is conserved. This explains the pinned lateral lattice constant we observed in our experiments.

depends on both oxygen pressure and temperature. Higher oxygen pressure and lower(!) temperatures increase the oxygen content x in the oxide. The convergence of x against its equilibrium value, however, happens faster at higher temperatures. It is reasonable to assume that this rule is also valid for thin films. We can conclude from our measurements that for thin films of 5 nm praseodymium oxide, an oxygen pressure of 1 atm, and a temperature of 200 °C, x does not increase significantly from 1.5 within 30 min. It does so, in contrast, at 300 °C and higher annealing temperatures.

Rudenko and Boganov³⁶ demonstrated that hexagonal praseodymium oxide only exists as stoichiometric Pr_2O_3 , whereas cubic Pr_2O_3 ought to be called $\text{Pr}_2\text{O}_{3+\delta}$ because it is only energetically favorable at this composition with excess oxygen. This explains the phase transition one observes when hexagonal Pr_2O_3 , which is our original phase after the evaporation process, is transformed to twin-free cubic Pr_2O_3 or $\text{Pr}_2\text{O}_{3+\delta}$ by annealing in nitrogen¹¹ or low pressure oxygen.¹² The phase transition and the formation of an interface layer were not observed after annealing in UHV.¹¹ If the substrate was oxidized before the evaporation process, the film grows in the cubic phase but with a high density of stacking twins. In general, the phase transition is only observed after an interfacial layer was formed between film and substrate.¹² This has been interpreted as a disconnection of film and substrate.¹² As we observed that the lateral lattice constant does not change significantly during the annealing process, this disconnection cannot be the reason for the phase transformation. In our opinion the reason for the transformation is as follows. During the annealing process the oxidation stage of the film is increased. The tendency of the oxygen atoms to bind with Si atoms rather than to increase the oxidation stage of the film is of course weakened as the interface silicate layer grows. When the interface layer is thick enough to serve as an adequate diffusion barrier, the

oxygen content in the oxide film is so high that the cubic structure of $\text{Pr}_2\text{O}_{3+\delta}$ is energetically favorable compared to the initial hexagonal structure of Pr_2O_3 , regardless of the fixed lateral lattice constant, which favors the hexagonal structure.

Rudenko and Boganov³⁶ noted that even very small values of δ make the hexagonal structure energetically disadvantageous so that $c\text{-Pr}_2\text{O}_{3+\delta}$ with bixbyite structure is formed. Therefore, it is also possible that the critical oxygen content for the phase transformation is already reached before the oxygen atoms bind with the Si substrate and form the interface layer. To pinpoint which of the two models is correct, further *in situ* studies are necessary.

During the annealing experiments presented here, the oxygen pressure is so high that a further oxidation from $\text{Pr}_2\text{O}_{3+\delta}$ toward the formation of PrO_2 and $\text{PrO}_{2-\delta}$ takes place. Having built up the silicate as a diffusion barrier, the Pr_2O_3 with cubic structure is further oxidized to PrO_2 . This, however, is only the case for annealing temperatures of more than 200 °C. At lower temperatures, no phase transformation occurs because the oxidation process of the praseodymia film is so slow that the oxygen content does not increase significantly from Pr_2O_3 during the given annealing time of 30 min.

The appearance of oxygen vacancies in all films presented here is also better understandable if we include the results from Hyde *et al.*³⁴ and Burnham and Eyring³⁵ for bulk PrO_x . They reported that for annealing temperatures significantly above 300 °C, x converges toward values smaller than two so that the full stoichiometric PrO_2 cannot be obtained. For lower temperatures, convergence takes place very slowly so that it takes days to reach stoichiometric PrO_2 .^{34,35} At $T_A < 500$ °C, however, there is a miscibility gap between PrO_2 and $\text{PrO}_{1.83}$, which can be assigned as PrO_2 with ordered oxygen vacancies, for bulk praseodymia. That means that the oxidation stages with $1.83 < x < 2$ are energetically unfavorable at these temperatures and phase separation takes place. These results are supported by Rudenko and Boganov,³⁶ who showed that it is difficult to achieve stoichiometric bulk PrO_2 when annealing in 1 atm oxygen atmosphere and that praseodymium oxide tends to coexist in different oxidation stages, while true stoichiometry is the exception rather than the rule.³⁶ They also stated that the intermediate phases between PrO_2 and cubic Pr_2O_3 are essentially superstructures formed by ordering of oxygen vacancies in the PrO_2 lattice. As we showed that for thin praseodymia films on Si(111) strain effects occur due to the fixed lateral lattice constant, it is evident that the ordering of those oxygen vacancies can be different for thin films compared to the ordering in bulk praseodymia. A vertical but not horizontal ordering of oxygen vacancies was reported in Ref. 16. The characteristic peak for this ordering of oxygen vacancies at $L \approx 1.5$ on the specular rod is also visible for some of the samples annealed at above 200 °C and investigated here, although the intensity of this peak varies from sample to sample. The observation that praseodymium oxide tends to coexist in different oxidation stages also reconfirms that the coexisting $\text{PrO}_{2-\delta}$ and PrO_2 we observed in our thin films are the rule rather than the exception. However, time and

oxygen mobility are not always sufficient to form a stoichiometric phase. The result is that parts of the film are under stoichiometric $\text{PrO}_{2-\delta}$.

We cannot exclude that a loss of oxygen occurs during the time between sample preparation and x-ray measurements of several days. However, this possibility seems improbable to explain the entire observed effect because the kinetics of the oxidation process, at least for bulk praseodymia, decrease significantly at temperatures of $T_A \leq 200^\circ\text{C}$.³⁴ We also showed above that the oxidation of thin films from $h\text{-Pr}_2\text{O}_3$ to PrO_2 of *thin films* does not take place within 30 min at $T_A \leq 200^\circ\text{C}$, indicating that the kinetics of thin films are similar to the ones of bulk praseodymia. Thus we assume that no significant change in the stoichiometry takes place at room temperature.

We also observed that the vertical layer distance varies significantly for different samples and different annealing temperatures, whereas the lateral lattice constant is always very close to the value of bulk $h\text{-Pr}_2\text{O}_3$. This is true for both the PrO_2 and the $\text{PrO}_{2-\delta}$ parts of the film. In our opinion the reason for this is that the initial praseodymium sesquioxide film crystallizes in the hexagonal phase during the evaporation process. The lateral ordering at the interface seems to be fixed by the substrate. If no long range reordering of the praseodymium atoms is possible, short range reordering allows the formation of the cubic $(111)_B$ -oriented unit cell. A change in the lateral lattice constant, however, requires a long range reordering of the praseodymium ions or the formation of additional interface dislocations. Obviously, additional interface dislocations are not formed during the phase transformation from $h\text{-Pr}_2\text{O}_3$ to PrO_2 . The assumption that such long range reordering does not take place was confirmed by Zaumseil in Ref. 30, who also reported a nonbulk in-plane lattice constant of 0.3849 nm for $\text{PrO}_2/\text{Si}(111)$. This value is slightly smaller than the value we observe in our experiments. In addition Zaumseil³⁰ reported that the vertical layer distance of PrO_2 films on $\text{Si}(111)$ is $d=0.310$ nm. This value agrees well with the layer distance we observe for the stoichiometric PrO_2 phase. Zaumseil³⁰ did not report on the nonstoichiometric $\text{PrO}_{2-\delta}$ phase. Probably the resolution of the experiment was not sufficient to discern both species.

At any rate, strain as it is found in the samples studied in this work energetically prefers $\text{PrO}_{2-\delta}$ versus PrO_2 because oxygen vacancies increase the radius of the praseodymium ions and the unit cell of the oxide and thus lessens the lattice mismatch to the hexagonal lateral layer distance (cf. Fig. 9). The vertical lattice constants of both the PrO_2 and the $\text{PrO}_{2-\delta}$ phase are also influenced by the lateral strain. Thus we observe that the lattice constant of the PrO_2 part of the film is smaller than the bulk value.

The vertical layer distance of the $\text{PrO}_{2-\delta}$ phase is close to the layer distance of $\text{PrO}_{1.83}$ and strained $\text{PrO}_{1.83}$, although there is a tendency to smaller values for higher annealing temperatures. The lattice constant of $\text{PrO}_{1.83}$ is derived from bulk Pr_6O_{11} . However, we call the structure $\text{PrO}_{1.83}$ because the $\text{PrO}_{2-\delta}$ structure cannot be a cubic structure (such as Pr_6O_{11}), as in some cases it shows superstructures only in vertical but not in lateral direction. In bulk structures, there is a miscibility gap between PrO_2 and $\text{PrO}_{1.83} \triangleq \text{Pr}_6\text{O}_{11}$. It is not

clear whether the same miscibility gap exists in thin films, but we include the lattice constants of strained and unstrained $\text{PrO}_{1.83}$ as orientation. The lattice constant of $\text{PrO}_{2-\delta}$ seems to be close to the structure of $\text{PrO}_{1.83}$. Probably the structure is stabilized by the good lateral lattice matching to the former $h\text{-Pr}_2\text{O}_3$ film (cf. Fig. 9).

The decreasing layer distances of samples annealed at higher temperatures, which were shown in Fig. 10, indicate that these samples have fewer oxygen vacancies compared to samples annealed at lower temperatures (but high enough to transform from hexagonal to cubic structure). This may be counterintuitive if compared to the results obtained for bulk praseodymia.³⁴ As we already mentioned, the equilibrium oxidation stage of praseodymia is lower at higher temperatures at a given oxygen pressure. 30 min should be sufficient to reach the final oxidation stage of the film at $T_A \geq 500^\circ\text{C}$. Thus we should observe higher layer distances at higher temperatures. We observe, however, a further reduction in the layer distances at higher temperatures. In our opinion, the reason for this is the different cooling process. Because the temperature of the sample holder is higher at higher annealing temperatures, the holder serves as a heat source for the sample during the cooling process, which is more slowly for the samples that were annealed at higher temperatures. This leads to further oxidation of the film at lower temperatures during the cooling process, since the cooling is performed in oxygen atmosphere. Thus it appears that both the annealing temperature and details of the cooling process of the samples are very important, as during the cooling process the oxidation stage of the film increases and thus the number of oxygen vacancies decreases.

Rudenko and Boganov³⁶ also underline the importance of the cooling process after annealing in oxygen to obtain bulk PrO_2 and suggested a cooling rate of 20°C/h at $500^\circ\text{C} \rightarrow 400^\circ\text{C}$ and even slower down to 200°C . These values are for bulk praseodymium oxide. It is not clear what cooling rate is adequate for thin films, but the values for bulk praseodymia provide a decent basis. The cooling rate at the relevant temperatures (of more than 200°C) in this work was significantly higher and can be estimated to 25°C/min . The effect of different temperature ramps and/or oxygen pressure for PDA of thin films will be a matter of our future work.

V. SUMMARY

In summary, B -oriented $Fm\bar{3}m$ praseodymium oxide films on $\text{Si}(111)$ were verified after PDA of $h\text{-Pr}_2\text{O}_3$ films in high pressure oxygen at temperatures from 300 to 700°C . The films are free of residual grains of hexagonal and cubic Pr_2O_3 and consist of two species, namely, PrO_2 and $\text{PrO}_{2-\delta}$, which coexist laterally. The vertical lattice constant decreases by several percent if the annealing temperature is increased, whereas the lateral lattice constant is almost identical to the lateral lattice constant of $h\text{-Pr}_2\text{O}_3$. As similar behavior was reported for $c\text{-Pr}_2\text{O}_3$ films, we assume that the lateral lattice constant is pinned throughout the annealing process of thin praseodymium oxide films and does not depend on the final stoichiometry of the oxide film. The prob-

able reason for this is that no long range reordering of the praseodymium atoms takes place during the annealing process. Samples that were annealed at 100 and 200 °C were still purely hexagonal. So the phase transition occurs between 200 and 300 °C within 30 min of annealing in 1 atm oxygen atmosphere.

Oxygen vacancies were found in each of the PrO₂ samples since the PrO_{2-δ} phase has a larger layer distance than expected for both bulk PrO₂ and tetragonally strained PrO₂. Some of the investigated samples show additional peaks at $L \approx 1.5$ on the specular rod, pointing to a twice as large as expected vertical unit cell due to at least partly periodical ordering of these oxygen vacancies in vertical direction. No clear temperature dependency was observed for this periodical ordering.

Praseodymium oxide, as well as other lanthanide oxides, forms interfacial silicate layers on Si substrates when annealed to several hundred degree Celsius. Here, a quantitative analysis of the Pr-rich silicate layer thickness is given. The silicate layer builds up during PDA at 500 °C or higher, and its size increases significantly with increasing annealing temperatures.

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