Structure and stability of cub-Pr₂O₃ films on Si(111) under post deposition annealing conditions

S. Gevers¹, T. Weisemoeller¹, B. Zimmermann¹, C. Deiter², J. Wollschläger^{*,1}

¹ Fachbereich Physik, Universität Osnabrück and Center of Interface Science, Barbarastrasse 7, D-49069 Osnabrück, Germany

² HASYLAB at DESY, Notkestrasse 85, D-22607 Hamburg, Germany

Received XXXX, revised XXXX, accepted XXXX

Published online XXXX

PACS 61.05.cm, 61.05.cp, 61.05.jh, 68.35.ct, 68.55.-a, 81.15.Hi

* Corresponding author: e-mail Joachim.Wollschlaeger@uos.de, Phone: +49-541-9692651

Ultra thin heteroepitaxial Pr₂O₃ films on Si(111) were characterized by X-ray diffraction and X-ray reflectometry to determine the film and interface structure. These results exhibit two oxide phases within the praseodymia film after preparation which can be assigned to different oxygen stoichiometries. After post deposition annealing of the films at different temperatures up to 600 °C the surface was studied by spot profile analysis low energy electron diffraction, with regard to the stability of the film surface.

The results show that terraces with mono-atomic step heights and mosaics can be found at the film surfaces after annealing at 300 °C. Higher annealing temperatures do not cause further changes of structure and morphology except of a slight increase of the mosaic spread due to lateral strain effects within the oxide film. These results indicate that the films are stable at temperatures as high as 600 °C.

Copyright line will be provided by the publisher

1 Introduction It is one of the main goals in today's micro- and nanoelectronics to combine the technologically dominating Si wafer platform with alternative semiconductor materials like Ge in order to create integrated devices with higher performance and extended functionality. High quality praseodymia films are interesting within this field because they can be used as buffer material between Si substrates and Ge layers (germanium-on-insulator technology, GOI). This provides applications of high interest like the cost-effective integration of III-V optoelectronic materials (GaAs) on the Si material platform [1,2]. In addition, the formation of Ge nanodots on top of cubic-Pr₂O₃ films was studied as a model system for Ge nanocrystal based non-volatile memory (NVM) cells [3]. Cubic-Pr₂O₃ was chosen as insulating buffer material because the cubic (bixbyite) structure fits the cubic (diamond) structure of Si and Ge. Furthermore, the lattice constant *a* of cubic-Pr₂O₃ lies between twice of the lattice constants of silicon and germanium (2*a*_{Si} and 2*a*_{Ge}, respectively). All these applications demand high temperatures up to

600 °C during the growth process of the multi-layer structure or during post deposition treatments. Therefore it is necessary to verify the structural stability of praseodymia films in order to assure the growth of high quality Ge structures. For this purpose, we report on X-ray diffraction (XRD) as well as X-ray reflectometry (XRR) studies which were performed directly after film preparation to determine the initial film structure. Afterwards, the structural stability of the film surface was investigated by spot profile low energy electron diffraction (SPA-LEED) during post deposition annealing (PDA) under UHV conditions.

2 Experiment Ultra thin films of hexagonal Pr₂O₃ (hex-Pr₂O₃) structure were deposited on clean boron-doped Si(111) substrates as reported in [4,5]. These samples were annealed in 1 atm N₂ at 600 °C for 30 minutes in order to create heteroepitaxial Pr₂O₃ films with cubic bixbyite structure (cub-Pr₂O₃) [4]. XRR measurements provide average film thicknesses of 4 nm (sample A) and 9 nm (sample B).

Copyright line will be provided by the publisher

X-ray measurements for determination of the oxide film structure were performed at beam line W1/HASYLAB. A six circle diffractometer and a photon energy of 10.5 keV were used to conduct XRR and XRD measurements. In both cases the data were recorded with $\theta - 2\theta$ scans.

Afterwards, the samples were annealed in ultra high vacuum (UHV, base pressure 10^{-10} mbar) at temperatures from $T = 300^\circ\text{C}$ up to 600°C (PDA, with steps $\Delta T_A = 100 \pm 30^\circ\text{C}$ for the annealing temperature). The annealing was performed by resistive heating of the samples.

In situ SPA-LEED investigations were carried out in order to study the surface structure and morphology. These measurements were performed after each annealing step. Furthermore, energy dependent measurements of the specular diffraction peak intensity were made to characterize the surface morphology of the oxide films by spot profile analysis.

3 Results

3.1 XRD Figure 1 shows the θ - 2θ scans of the 4 nm (thick red lines) and 9 nm (thin blue lines) praseodymia films after annealing in N₂ for 30 min. The scaled scattering vector $L = K_\perp d_{Si}/2\pi$ ($K_\perp$ = vertical component of the scattering vector, $d_{Si} = 0.3135$ nm layer distance of the Si(111) substrate normal to the surface is given in reciprocal lattice units (r.l.u.). Thus the Bragg peaks denoted by $(00L)_S$ in surface notation are equivalent to the $(LLL)_B$ Bragg peaks in bulk notation due to the (111) orientation of the Si substrate.

Strong and sharp Si Bragg peaks can be observed at the integer L values due to the large penetration depth of the

X-ray beam through the *ultra thin* oxide film into the *semi infinite* silicon substrate. Additional Bragg peaks which are caused by the cub-Pr₂O₃ film are located close to both $L = 1$ and $L = 2$ due to the similar lattice constants.

Whereas the Si Bragg peak at $L = 1$ is allowed within the kinematic diffraction theory for the diamond structure of Si, the weaker peak at $L = 2$ is kinematically forbidden and caused only by non-spherical charge distributions of the Si atoms. Hence the region at $(001)_S$ is used to get information about the whole film structure (interface and crystalline part) due to the strong interference between film and substrate. For a closer look at only the crystalline part of the film, the region close to $(002)_S$ is preferred, because there is no significant interference between film and substrate and the praseodymia Bragg peak is also more separated from the (weak) Si peak.

A closer look at $L \approx 2$ shows that the praseodymia Bragg peaks obtained from both samples are shifted to lower L values compared to the Si peaks while they are shifted to larger values of L with respect to bulk cub-Pr₂O₃. Therefore the layer distance lies between the layer distance of both materials. In addition, the praseodymia Bragg peak is obviously asymmetric for the 4 nm film. This points to the coexistence of two oxide phases with different (vertical) lattice constants. Therefore, these data are carefully simulated within the kinematic diffraction theory to determine both lattice constants. The superposition of the diffraction from two oxide phases had also to be used to get good agreement with the experimental data for the 9 nm film. Thus, both praseodymia films separate in two phases with different vertical lattice constants. As it will be shown, one distance (d_{large}) is closer to the cub-Pr₂O₃ bulk value of 0.322 nm [6] and the other constant (d_{short}) is significantly smaller. This is in agreement with XRR experiments which confirm that both films split into two laterally coexisting parts of approximately the same film thickness.

For the smaller oxide film (sample A) the vertical lattice constants are determined to $d_{large} = 0.3198$ nm and $d_{short} = 0.3160$ nm with crystalline film thicknesses of $D_{large} = 4.5$ nm and $D_{short} = 3.8$ nm, respectively. Furthermore, the thicker praseodymia film (sample B) exhibits vertical lattice constants of $d_{large} = 0.3191$ nm and $d_{short} = 0.3173$ nm and crystalline film thicknesses of $D_{large} = 8.9$ nm and $D_{short} = 8.8$ nm, respectively.

Data close to $L = 1$ show explicit differences between the oxide films of both samples. The signal of sample A exhibits strong interference effects with considerable double oscillations (beating) which point to an amorphous interface layer with a similar thickness compared to the crystalline film [7]. Such double oscillations cannot be observed in the signal of sample B so that a more specific analysis is required.

The careful simulation of the data shows that the interface layer thickness (I) of sample A is slightly different for the two oxide species. They are within the thicknesses of the crystalline film with $I_{large} = 3.3$ nm and $I_{short} = 4.2$ nm

Figure 1 Specular XRD θ - 2θ scans of the praseodymia films on Si(111) at the region of the first (a) and second (b) silicon Bragg peaks. The thin solid lines represent the 4 nm praseodymia film and the thin lines the 9 nm film. The position of the bulk cub-Pr₂O₃ Bragg peaks are marked with vertical lines.

Figure 2 Two-dimensional SPALEED patterns of the 4 nm (a) and 9 nm (b) oxide films, obtained after annealing the samples at 500 °C in UHV. The crystallographic directions and denotations are given in (a) with respect to the cub-Pr₂O₃(111) surface.

and similar to the thickness of the crystalline oxide film causing the beating of the interference signal. Almost identical interface thicknesses are observed for sample B. They are $I_{large} = 4.0$ nm and $I_{short} = 3.9$ nm and half as small as the crystalline film thicknesses so that no beating is observed. XRR results show that about two mono layer of each interface have a significantly higher electron density which is closer to the density of cub-Pr₂O₃ than to the density of the Si substrate. This part is attributed to an amorphous silicate interface layer between the crystalline film and the residual part of the interface layer [12]. Finally, the decrease of both praseodymia signals at $L > 2$ compared to the signals at $L > 1$ contains a reference to mosaics within the crystalline film namely within the species with lower lattice constant.

3.2 SPA-LEED Figures 2 (a) and (b) show two-dimensional electron diffraction patterns of both praseodymia films recorded at an electron energy of 57.8 eV after annealing the samples at 500 °C.

Strong diffraction peaks with a three fold symmetry are visible in each diffraction pattern due to the cubic symmetry of the film. The distance between these peaks is approximately four times smaller than the size of the Si(111) surface Brillouin-Zone (SBZ). Therefore they can be attributed to cub-Pr₂O₃ because its surface unit cell (SUC) in real space is about four times bigger (bixbyite structure) than the unreconstructed Si(111). These diffraction patterns confirm the cub-Pr₂O₃ structure for the *surface* as demonstrated before by XRD for the as-prepared praseodymia *films*. The comparison between the diffraction patterns of both samples show that the peaks obtained from the 4 nm oxide film are sharper than the peaks of the 9 nm film which points to a higher defect density of the thicker cub-Pr₂O₃ film.

To get more information about the surface morphology a FWHM analysis of the (00)-diffraction peak was made for both samples at various vertical scattering vectors ($K_{\perp}$). The results are shown exemplarily in Figure 3 for the annealing step at 500 °C. Other annealing steps show comparable results. The analysis was done by fitting the (00)-diffraction peaks with single Lorentzian functions.

As shown in Figure 3 an oscillatory behavior of the FWHM can be observed for both samples. An additional linear increase is also visible. Generally speaking, the linear increase is due to mosaics while the oscillations of the FWHM are due to mono-atomic steps [8,9]. Figure 4 shows the obtained fitting parameters for different PDA steps. The mosaic spread (a) and the mean terrace widths (b) exhibit just one value for both samples, respectively. Compared to the XRD results it seems that only one oxide species remains at both samples after annealing. Furthermore, the oxide film surface of sample A shows a slightly lower mosaic spread during the whole annealing process compared the film surface of sample B. These values increase for both samples due to relaxation processes at higher annealing temperatures. The mean terrace widths of both surfaces stay nearly constant during the annealing process. Here, the 4 nm sample exhibits a higher average value with $\bar{L}_A = 19.3$ Å compared to $\bar{L}_B = 9.0$ Å of the 9 nm film, which confirms the higher defect density (mono-atomic steps) for the thicker film.

4 Discussion & Conclusion The initial film structure of both samples can be roughly described with a model which is similar to the one suggested for thin PrO₂ films on Si(111) earlier [9]. The crystalline praseodymia film splits into two phases with bixbyite structure and stoichiometry close to cub-Pr₂O₃. However, the bulk vertical lattice constant of 0.322 nm is larger than the values determined for both phases of the praseodymia film. Lateral strain effects which are described in [11] cannot explain this because they would lead to even greater vertical lattice constants compared to bulk cub-Pr₂O₃ [9]. Hence, this can be attributed to a higher oxygen amount within the praseodymia species as the initially assumed Pr₂O₃ stoichiometry since further oxidation of the Pr₂O₃ film leads to the formation of Pr⁴⁺ ions which have a smaller radius than Pr³⁺ ions [10]. Thus the lattice constant is de-

Figure 3 FWHM dependency of the (00) diffraction peaks against the scattering vector $K_{\perp}$ after annealing in UHV at 500 °C. Crossed and dotted markers represent the Praseodymia films with 4 nm and 9 nm thickness. For the 4 nm film the dashed line indicates a linear increase of the FWHM due to surface mosaics.

Figure 4 Data obtained from the FWHM analysis against the annealing temperatures: (a) mosaic spreads; (b) mean terrace widths.

creased with increasing oxygen content. We attribute this effect to a slight, increasing oxidation during our XRD experiments under ambient conditions, where Pr₆O₁₁ is the stable praseodymia phase.

Both species have similar film thicknesses which agree with the entire film thickness as determined by XRR. Therefore the species are separated laterally. As discussed in [13], a stoichiometric lattice composition is the exception rather than the rule. So that the formation of two non-stoichiometric cub-Pr₂O₃ phases under ambient conditions is probable.

Furthermore, an amorphous interface layer between film and substrate with a Pr-poor and a Pr-rich silicate structure is formed during the film preparation as reported in [12], too. The average thickness of this combined interface is approximately the same for both samples.

The diffraction patterns obtained with SPA-LEED show that both samples exhibit a cub-Pr₂O₃ structure at the surface after PDA. The surface morphology of both praseodymia films consists of mosaics and mono-atomic steps. This surface morphology has also been observed for annealed PrO₂ films [9]. However, these films had two different praseodymia phases at the surface after PDA, while we observe only one phase here. Due to this and due to the formation of clear cub-Pr₂O₃ diffraction spots which point to a highly ordered oxygen sublattice, we suggest that these praseodymia films are homogeneously reduced to pure cub-Pr₂O₃ while the films are partly oxidized under ambient conditions (cf. XRD results).

The 9 nm film shows a higher defect density caused by smaller terraces and higher mosaic angles. The origin of this effect can be found during the growth process

of the hex-Pr₂O₃ film. Here, higher film thicknesses ($D > 4.2$ nm) lead to a decrease of the domain size which reduces the lateral long-range order of the oxide film [5] and causes higher defect densities. The PDA of both samples at higher temperatures up to 600 °C slightly increases the mosaic angles of the crystal domains, whereas the mean terrace widths stay nearly constant.

It can be concluded that, despite the different oxide film thickness, both samples exhibit nearly the same structural properties after preparation. The results show that ultra thin cub-Pr₂O₃ films on Si(111) are stable and even purified during PDA processes up to 600 °C, so they are good candidates for post deposition treatments. Here, oxide films with small film thicknesses (less than 10 nm) seem to be more advantageous because of a lower defect density.

Acknowledgements The authors acknowledge the Deutsche Forschungsgemeinschaft (DFG) via Graduate College 695 for financial support as well as T. Schroeder and A. Guissani at the IHP GmbH, Frankfurt(Oder), Germany, for sample providing. Synchrotron experiments were carried out at HASYLAB/DESY. DESY is a member of the Helmholtz Association (HGF).

References

- [1] H. Tanoto, S.F. Yoon, W.K. Loke, E.A. Fitzgerald, C. Dohrman, B. Narayanan, M.T. Doan and C.H. Tung, *J. Vac. Sci. Technol.* **B 24**, 152 (2006).
- [2] A. Giussani, O. Seifarth, P. Rodenbach, H.-J. Muessig, P. Zaumseil, T. Weisemoeller, C. Deiter, J. Wollschläger, P. Storck and T. Schroeder, *J. Appl. Phys.* **103**, 084110 (2008).
- [3] T. Schroeder, I. Costina, A. Giussani, G. Weidner, O. Seifarth, Ch. Wenger and P. Zaumseil, *J. Appl. Phys.* **102**, 034107 (2007).
- [4] J.P. Liu P. Zaumseil, E. Bugiel and H.J. Osten, *Appl. Phys. Lett.* **79**, 671 (2008).
- [5] T. Schroeder, T.-L. Lee, L. Libralesso, I. Joumard and J. Zeegenhagen, *J. Appl. Phys.* **97**, 074906 (2005).
- [6] K.-H. Hellwege and A.M. Hellwege, eds., 1975 *Landolt-Börnstein: Numerical Data and Functional Relationships in Science and Technology (New Series); Group III: Crystal and Solid State Physics 7 (Crystal Structure Data of Inorganic Compounds)*, Volume edited by W. Pies and A. Weiss (Springer, Berlin, 1973).
- [7] T. Weisemoeller, F. Bertram, S. Gevers, C. Deiter, A. Greuling and J. Wollschläger, *Phys. Rev. B* **79**, 245422 (2009).
- [8] T.-M. Lu and M.G. Lagally, *Surf. Sci.* **120**, 47 (1982).
- [9] S. Gevers, T. Weisemoeller, B. Zimmermann, F. Bertram, C. Deiter and J. Wollschläger, *J. Phys.: Condens. Matter* **21**, 175408 (2009).
- [10] R. G. Haire and L. Eyring, *Handbook on the Physics and Chemistry of Rare Earths* **18** (Elsevier Science Ltd, 1994).
- [11] T. Weisemoeller, F. Bertram, S. Gevers, A. Greuling, C. Deiter, H. Tobergte, M. Neumann, A. Guissani, T. Schroeder and J. Wollschläger, *J. Appl. Phys.* (to be published).
- [12] T. Schroeder, P. Zaumseil, G. Weidner, Ch. Wenger, J. Dabrowski and H.-J. Muessig, *J. Appl. Phys.* **99**, 014101 (2006).
- [13] V.S. Rudenko and A.G. Boganov 1971, *Inorg. Mater. (USSR) (Engl. Transl.)* **1**, 98 (1971)