The influence of lattice oxygen on the initial growth behavior of heteroepitaxial Ge layers on single crystalline $\text{PrO}_2(111)/\text{Si}(111)$ support systems

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A combined structure and stoichiometry study on the growth behavior of single crystalline Ge(111) layers on $\text{PrO}_2(111)/\text{Si}(111)$ heterostructures is presented. *Ex situ* x-ray diffraction techniques indicate that the interaction between Ge and $\text{PrO}_2(111)$ results in a complete reduction of the buffer oxide to a cubic $\text{Pr}_2\text{O}_3(111)$ film structure. *In situ* reflection high energy electron diffraction, x-ray and ultraviolet photoelectron spectroscopy studies demonstrate that this chemical reduction of the oxide support occurs during the initial Ge growth stage. The interaction of PrO_2 with Ge results in the formation of an amorphous Ge oxide layer by the diffusion of lattice oxygen from the dielectric to the forming semiconductor deposit. After the complete conversion of PrO_2 to cubic Pr_2O_3 , the supply of reactive lattice oxygen is exhausted and the continuous Ge deposition reduces the initially formed amorphous GeO_2 -like film to GeO. The sublimation of volatile GeO uncovers the single crystalline cubic $\text{Pr}_2\text{O}_3(111)$ film surface which provides a thermodynamically stable template for elemental Ge heteroepitaxy. A Volmer–Weber growth mode is observed which results after island coalescence in the formation of atomically smooth, single crystalline Ge(111) layers. © 2008 American Institute of Physics. [DOI: 10.1063/1.2870270]

I. INTRODUCTION

The preparation of epitaxial germanium-on-insulator (GeOI) heterostructures on silicon (Si) attracts increasing research resources due to its high potential to improve the performance and/or functionality of future Si-based microelectronics. A main research field is hereby presented by innovative GeOI systems aiming to boost the sub-45 nm complementary metal-oxide-semiconductor (CMOS) technologies.^{1–3} For this purpose, high quality single crystalline Ge layers are grown on alternative high-*k* dielectric heterostructures on Si.^{4,5} Furthermore, GeOI on Si is of interest to achieve the cost-effective monolithic integration of III-V optoelectronic materials on the dominating Si material platform. For instance, GeOI systems are discussed as potential basis for the global integration of high quality GaAs layers on Si. This approach is promising because, in contrast to the large lattice ($\sim 4.1\%$) and thermal ($\sim 110\%$) mismatch between GaAs and Si, only a minimal lattice mismatch ($\sim 0.08\%$) and almost no thermal expansion coefficient difference are reported between GaAs and Ge.⁶

It must, however, be pointed out that, to the best of our knowledge, the quality of the up to nowadays available GeOI heterostructures on Si prepared by two simple, subsequent oxide and Ge epi-steps have not yet achieved the level of technological relevance. This is mainly due to the fact that the fundamental physical mechanisms of the interaction between Ge and the buffer dielectric materials (i.e., transition

and rare earth oxides) are only poorly understood at present. Typical unsolved solid state issues, governing the structural and in consequence electrical properties of such GeOI systems, concern, for example, the thermodynamic stability of Ge in contact with transition and rare earth (RE) buffer dielectrics, the control of the growth mode to achieve closed Ge layer structures, the mechanisms at work in the creation of defects in the Ge film, the possibility of preparing strained Ge layers by heteroepitaxial overgrowth of lattice mismatched oxide buffers, etc.

In this respect, the results of a combined structure-stoichiometry study on the epitaxial growth of Ge on single crystalline $\text{PrO}_2(111)/\text{Si}(111)$ systems is reported in the present paper to shed light on the widely unknown interaction of epitaxial Ge systems with RE oxide heterostructures on Si(111). Here, the $\text{PrO}_2(111)/\text{Si}(111)$ support system was chosen as substrate for Ge heteroepitaxy for the following reasons: First, as reported in an earlier work for the similar cubic (cub) $\text{Pr}_2\text{O}_3(111)/\text{Si}(111)$ system,⁷ it was recently demonstrated that also single crystalline $\text{PrO}_2(111)$ films can be prepared with an exclusive type-B stacking sequence on Si(111) substrates.⁸ Second, the PrO_2 unit cell ($a = 0.5392$ nm) is only by 0.7% smaller than the Si bulk crystal ($a = 0.5430$ nm) so that it matches the Si(111) unit cell on the basis of a (1×1) coincidence lattice. In consequence, $\text{PrO}_2(111)$ films can be grown on Si(111) free of growth antiphase boundaries⁹ (gAPBs) and, due to the occupation of all tetrahedral sites by cations in the fluorite PrO_2 lattice, even free of cation antiphase boundaries (cAPBs).¹⁰ This situation is advantageous for the preparation of high quality

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dielectric heterostructures with low defect levels. For comparison, RE oxide heterostructures based on the bixbyite structure match the Si substrate on the basis of a (2×2) coincidence lattice with consequent low cation ordering symmetry, making the epitaxial RE_2O_3 films susceptible for the formation of gAPB as well as cAPB defects.^{9,11,12}

II. EXPERIMENT

Boron-doped 4 in. Si (111) substrates ($\rho = 5\text{--}15\ \Omega\text{ cm}$) were cleaned by the standard Piranha etch procedure.¹³ Additionally, the Si(111) wafers were etched for 30 min in 40% NH_4F and rinsed for 10 min in de-ionized water to prepare atomically smooth surfaces.¹⁴ Then the samples were loaded in the prechamber of the molecular beam epitaxy (MBE) machine, where a 200 °C annealing for 20 min with a pressure in the 10^{-6} mbar range was applied to outgas atmospheric contaminations. The H-terminated Si(111) wafers were subsequently brought into the ultrahigh vacuum (UHV) chamber (base pressure $\sim 10^{-10}$ mbar) and were annealed prior to oxide deposition for 5 min at 700 °C to prepare high quality (7×7) -Si(111) surfaces.¹⁵ A 10 nm thick, single crystalline hexagonal (hex) $\text{Pr}_2\text{O}_3(0001)$ film was grown on Si(111) by MBE at a substrate temperature of 625 °C and a flux of 0.1 nm/s, using highly purified Pr_6O_{11} source material.¹⁶ To prepare $\text{PrO}_2(111)$ films on Si(111), an *ex situ* annealing step in an atmosphere of 1 bar O_2 for 30 min at 450 °C is required to (a) induce the hex- to cub- Pr_2O_3 phase transition⁷ and (b) further oxidize the cub- Pr_2O_3 film to PrO_2 .⁸ Prior to Ge deposition, the sample was cleaned again by an annealing step, namely, the outgas step in the MBE prechamber at 200 °C for 20 min. Ge was then deposited on the $\text{PrO}_2(111)/\text{Si}(111)$ support system at a temperature of 550 °C and a flux of 0.15 nm/s. It is noted that deposition at lower temperatures resulted in non-single crystalline, i.e. twinned Ge(111) films. The Ge growth was followed *in situ* step by step with x-ray and ultraviolet photoelectron spectroscopies (XPS and UPS), using nonmonochromatized Al $K\alpha$ (1486.6 eV) and He I (21.2 eV) radiation sources, respectively. A PHI 10-360 energy analyzer was used to collect the photoelectrons at a take-off angle of 45°. The XPS and UPS binding energy (BE) scales were calibrated with respect to the Au $4f_{7/2}$ core level (84 eV) and the valence band (VB) onset of Ge, respectively. Moreover, the UPS spectra were normalized with respect to the area to account for possible changes of the He I photon flux. It can be deduced from the atomic subshell photoionization cross sections of the VB states of the Ge/Pr oxide system at 21.2 eV ($\sigma[10^6\text{ barns}]$: O $2p=10.67$, Ge $4s=0.02$, Ge $4p=1.53$, and Pr $4f=0.68$) (Ref. 17) that the He I UPS VB study mostly reflects the O $2p$ partial density of states (pDOS).

An EK 35 reflection high energy electron diffraction (RHEED) apparatus from STAIB Instruments was employed to monitor the film growth along the $\langle 1\text{-}10 \rangle$ azimuth during continuous deposition, using a beam energy of 15.8 keV and an angle of incidence of the electron beam on the sample surface of about 2°.

Finally, in order to study the crystal phases and the epitaxial relationships, *ex situ* XRD techniques were applied.

FIG. 1. Specular θ - 2θ scans on the Pr oxide/Si(111) support system before (a) and after Ge deposition (b).

First, specular θ - 2θ scans with the scattering vector parallel to the Si substrate $[111]$ surface normal were performed at IHP laboratories with a Rigaku DMax1500 diffractometer, using Cu $K\alpha$ radiation ($\lambda=0.154\text{ nm}$). Furthermore, synchrotron radiation grazing incidence XRD (SR-GIXRD) in-plane measurements were carried out with an incidence angle α of 0.8° at the Hamburger Synchrotron Laboratory (HASYLAB) beamline BW2 with a beam energy of 10.5 keV ($\lambda=0.118\text{ nm}$).

III. RESULTS

A. XRD

The vertical growth direction of the Ge/Pr oxide/Si(111) heterostructure was determined by specular θ - 2θ XRD scans, as depicted in Fig. 1.

Plot 1(a) refers to the Si(111)/Pr oxide support system after the *ex situ* annealing in O_2 . The Si substrate orientation results in the presence of (111), (222), and (333) Si Bragg peaks, highlighted by dotted lines in the picture. With increasing 2θ angle, these peaks become more and more asymmetric on their right side. This is due to the diminishing overlap with broad Pr oxide reflections whose positions are representative of a PrO_2 phase. The bulk positions of $\text{PrO}_2(111)$, (222), (333) Bragg peaks are indicated in Fig. 1 by dashed lines ($2\theta=28.652^\circ$, 59.324° , and 95.859° , respectively). It is evident that the detected oxide reflections reproduce well the expected specular θ - 2θ XRD pattern of a (111) oriented PrO_2 phase but the experimentally found peak positions ($2\theta=28.9^\circ$, 60.0° , and 97.3° , respectively) are shifted to higher 2θ angles, indicating a compression of the (111) lattice spacing in the PrO_2 phase of about 1%. A possible explanation of this experimental finding might be given by strain effects. Bulk values predict an in-plane tensile strain in the PrO_2 lattice on Si due to the negative lattice mismatch of about 0.7% between film and substrate which could well result in a vertical compression of the PrO_2 (111) planes. It must, however, be stated that other reasons cannot be ruled out, for example, the presence of an O-deficient PrO_2 phase. Indeed, it is well acknowledged that the stoichiometric fluorite structure PrO_2 exists only under positive oxygen pressure^{18,19} and that, according to the Pr-O phase diagram,

FIG. 2. In-plane scans ($L=0.05$; $\alpha=0.8^\circ$) along the $\text{Si}^{\text{surf}}[100]$ direction ($\text{Si}^{\text{bulk}}[11-2]$ azimuth) on the Pr oxide/Si(111) support system before (a) and after Ge deposition (b).

in the reduction process a number of oxygen-deficient $\text{PrO}_{2-\delta}$ phases ($0 < \delta < 0.20$) might form with bulk unit cell lattice parameters slightly smaller than Si.^{20–22}

Interestingly, the specular θ -2 θ XRD plot 1(b) after Ge deposition is substantially different from spectrum 1(a). First, in addition to the Si substrate reflections mentioned above, Ge(111), (222), and (333) Bragg peaks show up (solid lines), pointing to the growth of a single crystalline Ge epilayer with (111) orientation. Second, the PrO_2 Bragg peaks have all vanished. This is best visible in the vicinity of the forbidden Si(222) reflection. Recalling that the Ge(222) Bragg peak is also forbidden, it becomes obvious that the strong diffraction signal at this position might result from a superimposed Pr oxide signal. The observed specular θ -2 θ XRD pattern is indeed in line with the presence of (111) oriented cub- Pr_2O_3 phase underneath the Ge epilayer, as depicted in Fig. 1(b) by the dashed-dotted lines which indicate the positions of allowed cub- Pr_2O_3 (222), (444), and (666) Bragg peaks.

To unambiguously prove the chemical reduction of the PrO_2 (111) phase towards a cub- Pr_2O_3 (111) crystal structure in course of Ge film growth, SR-GIXRD in-plane studies along the $\text{Si}^{\text{surf}}[100]$ direction ($\text{Si}^{\text{bulk}}[11-2]$ azimuth²³) are reported in Fig. 2. At this point it is useful to introduce the type-A/type-B nomenclature of fcc-related heterostructures on Si(111), which will be widely used in the rest of the paper. Type A refers to the case in which the (111) layers of the grown film exhibit the same stacking vector as the Si(111) substrate; type B instead refers to the case in which a stacking fault at the epilayer/Si(111) interface rotates the stacking vector in the grown film by 180° around the Si(111) surface normal.^{24–27} In XRD in-plane scans, the type-A (type-B) orientation of an epitaxial layer results in a parallel (antiparallel) notation of its azimuths with respect to the Si(111) substrate.

Plot 2(a) refers to the sample before Ge deposition where three diffraction signals are detected in the scan from $H^{\text{surf}}=0.9$ to $H^{\text{surf}}=3.5$. The two features at $H^{\text{surf}}=1$ and 2 are crystal truncation rods (CTRs) from the Si substrate but the sharp spike at $H^{\text{surf}}=3$ is a true bulk Si Bragg peak, namely, the Si(22-4) reflection. It is seen that the Si(22-4) Bragg peak

at $H^{\text{surf}}=3$ is accompanied towards smaller reciprocal space values by the strong PrO_2 (-2-24) in-plane reflection which is centered at $H^{\text{surf}}=2.990$. As was the case in Fig. 1(a) for the specular θ -2 θ XRD scan, the oxide Bragg peak distribution in the in-plane study of Fig. 2(a) is in line with the presence of a fluorite PrO_2 phase but the experimentally detected peaks deviate from the expected bulk positions. The PrO_2 (-2-24) Bragg of truly stoichiometric PrO_2 is theoretically expected to be centered at higher reciprocal space values (theory: $H^{\text{surf}}=3.021$) than the Si(22-4) Bragg peak ($H^{\text{surf}}=3$) due to the $\sim 0.7\%$ smaller in-plane lattice with respect to Si. The fact that the experimental position of the PrO_2 (-2-24) Bragg peak is observed at even smaller reciprocal space values ($H^{\text{surf}}=2.990$) than the Si(22-4) Bragg peak ($H^{\text{surf}}=3$) shows that stress effects only play a minor role in the determination of the PrO_2 in-plane lattice spacing but that probably the formation of an oxygen-deficient $\text{PrO}_{2-\delta}$ phase ($0 < \delta < 0.20$) occurred. Detailed SR-GIXRD studies on the $\text{PrO}_{2-\delta}$ film properties on Si(111) as a function of preparation conditions are currently under way and will be presented elsewhere.⁸ Here, it is only noted that Weisemöller *et al.* succeeded to prove by SR-GIXRD studies the presence of an exclusively type-B oriented $\text{PrO}_{2-\delta}$ (111) film structure on Si(111),⁸ a result further corroborated in this work by the RHEED analysis below. In the rest of the paper, the single crystalline $\text{PrO}_{2-\delta}$ (111) film structure is briefly denoted PrO_2 (111) to express, in particular, the fluorite crystal symmetry of the oxide heterostructure before Ge deposition.

After Ge film deposition [plot 2(b)], the weak Si CTRs at $H^{\text{surf}}=1$ and 2 are not detected anymore so that the only visible Si substrate signal in the in-plane scan is the strong Si(22-4) Bragg peak at $H^{\text{surf}}=3$. The growth of a single crystalline Ge(111) layer can be derived from the observation of CTR peaks at $H^{\text{surf}}=0.960$ and 1.920 but, in particular, from the presence of the strong Ge(22-4) Bragg peak at $H^{\text{surf}}=2.880$ (theory: $H^{\text{surf}}=2.880$). This result confirms the presence of a fully relaxed Ge(111) film structure with the Ge $\langle 11-2 \rangle$ azimuth aligned along the oxide $\langle -1-12 \rangle$ in-plane direction. Certainly, this relationship corresponds to a type-A epitaxy of the Ge film with respect to the Si(111) substrate which cannot be derived from the here presented specular θ -2 θ and in-plane XRD study alone but will be proven in the discussion of the RHEED data below. Concerning the Pr oxide support, three new Pr oxide diffraction signals show up after Ge deposition in the in-plane SR-GIXRD plot 2(b). This result confirms the modification of the crystal symmetry of the dielectric buffer heterostructure during the deposition of Ge, namely, the chemical reduction of the initially PrO_2 -like phase (space group $Fm-3m$, No. 225) towards a cub- Pr_2O_3 crystal film structure (space group $Ia-3$, No. 206). This is true because the newly appearing three oxide Bragg peaks after Ge deposition at $H^{\text{surf}}=1.466$, 2.199 , and 2.932 can unambiguously be assigned to cub- Pr_2O_3 (-2-24), (-3-36), and (-4-48) Bragg peaks, respectively. The measured oxide reflections show up at higher H^{surf} values than expected from theory ($H^{\text{surf}}=1.461$, 2.191 , and 2.921 , respectively), probably due to strain effects in the oxide lattice induced by the smaller Si substrate underneath. To shed light on the mechanism of the chemical reduction of the Pr oxide

FIG. 3. *In situ* RHEED study of Ge growth on Pr oxide versus Ge deposition time. Long arrows indicate the position of the $[0.0.L]$ rod; in (h) the short arrows indicate the $c(2 \times 8)$ reconstruction of the Ge(111) surface.

support in the first growth stages of Ge, an *in situ* RHEED, XPS, and UPS study is presented in the following.

B. RHEED

The Ge growth on the Pr oxide support was monitored *in situ* by RHEED studies with the electron beam aligned along a Si $\langle 1-10 \rangle$ in-plane direction (Fig. 3). The RHEED image 3(a) of the clean $\text{PrO}_2(111)$ surface is characterized by a good signal to noise ratio, indicating a high degree of crystalline order. The pattern exhibits a weak streaky nature, pointing to a certain flatness of the oxide surface. The clearly visible intensity modulation along the rods, however, demonstrates that the $\text{PrO}_2(111)$ surface flatness is limited by the presence of oxide islands. Interestingly, the observed transmission pattern, created by the penetration of the RHEED electron beam through the oxide islands, allows to gain more information about the crystalline structure of the $\text{PrO}_2(111)$ film. The observed asymmetric arrangement of the Bragg peaks on parallel inclined lines [one of which is highlighted in Fig. 3(a) by a dashed line] is characteristic of the diffraction pattern of (111) oriented fluorite crystal structures imaged along a $\langle 1-10 \rangle$ azimuth.²⁶ Especially, the fact that no mirror symmetry plane is spanned in pattern 3(a) by the $[0.0.L]$ rod (arrow) and the $\langle 1-10 \rangle$ azimuth (electron beam direction) points to a $\text{PrO}_2(111)$ film free of stacking twins. This RHEED observation is in line with the above mentioned SR-GIXRD studies by Weisemoeller *et al.* on the $\text{PrO}_2(111)/\text{Si}(111)$ system⁸ which prove the exclusive

type-B orientation of the oxide films on the Si(111) substrate, a result furthermore in agreement with former studies on the similar $\text{cub-Pr}_2\text{O}_3(111)/\text{Si}(111)$ system.⁷ Images 3(b) and 3(c) report the status of the sample surface after 8 and 16 s of Ge deposition, respectively. A significant degradation of the signal to noise ratio is observed with respect to pattern 3(a), induced in particular by a strong increase of the diffuse background intensity. As discussed below in the XPS and UPS section, this experimental observation results from the formation of amorphous Ge oxides on the surface during the initial Ge growth stages on the $\text{PrO}_2(111)$ surface. A further substantial change in the RHEED image is detected after 48 s of Ge evaporation. A high signal to noise ratio is recovered in image 3(d) and the pattern turns very spotty. The extreme surface roughness can be attributed to the formation of single crystalline Ge(111) islands on the Pr oxide surface as a result of a Volmer–Weber growth mode, recently reported for self-assembled Ge nanocluster structures on cubic Pr oxide films by a multitechnique thin film study.²⁸ Due to the presence of two (111) oriented cubic fcc-related crystal structures on the sample, namely, the Ge deposit and the Pr oxide support, image 3(d) can be best described by the superposition of two similar types of spot patterns which however differ by their epitaxial orientation. The weaker spot pattern can be assigned to the Bragg peaks of uncovered Pr oxide regions which are arranged on the above described inclined line structures with the orientation depicted by the dashed line. The more intense spot pattern results from the growing Ge deposit which is again organized in form of inclined lines of the type mentioned above, but with an orientation given by the dotted line. As each of these spot patterns can be superimposed on the other one by a 180° rotation around the $[0.0.L]$ rod (arrow), RHEED image 3(d) demonstrates the starting growth of a type-A stacked Ge(111) structure on the type-B oriented cubic Pr oxide surface. It must, however, be noted that the eventual presence of type-B oriented Ge twins cannot be excluded by RHEED studies alone due to the possible overlap of the expected type-B Ge Bragg peaks with the Pr oxide pattern. However, a recent anomalous SR-GIXRD study on the Volmer–Weber growth mode of Ge nanoclusters on Pr oxide supports confirmed the absence of type-B oriented Ge rotational twins during the initial deposition stages and, thus, fully supports the here given description.²⁸ Images 3(e), 3(f) and 3(g) report the RHEED patterns after 56, 104, and 284 s of Ge deposition, respectively. These pictures demonstrate the further development of a rough Ge island structure on the Pr oxide surface and are characterized by the transition towards a pure type-A Ge Bragg peak RHEED pattern, as indicated in image 3(g) by the dotted line. This result demonstrates that the growth front of the Ge structure on the cubic Pr oxide support starts smoothing after 284 s of Ge deposition and a flat epi-Ge structure starts forming. Figure 3(h) reports the RHEED picture of a closed Ge(111) layer as a reference, obtained after a longer Ge deposition time. The observed streaky pattern without any pronounced intensity modulation along the rods proves the growth of a very flat epitaxial Ge(111) layer structure. Interestingly, half-order streaks [short arrows in image 3(h)] are observed between the Ge bulk unit cell rods which

FIG. 4. Ge 3d (a), O 1s (b), and Pr 3d_{5/2} (c) XPS spectra vs Ge evaporation time.

probably result from the formation a $c(2 \times 8)$ surface reconstruction on the epi-Ge(111) film structure.^{29–31}

C. XPS

Figure 4(a) shows the evolution of the Ge 3d peak during the epitaxial growth process on the PrO₂/Si(111) support system. Spectrum (1) refers to the clean PrO₂(111) surface.

The only feature which can be distinguished from the background is the Pr 5s peak situated at 37.2 eV.³² This feature is detected up to very high nominal Ge thicknesses [deposition steps (1)–(6)], in line with the Volmer–Weber growth mode of Ge on Pr oxides recently reported by Schroeder *et al.*²⁸ In spectrum (2), after 8 s of Ge deposition, the Ge 3d peak shows up at 32.4 eV. In the literature, the Ge 3d peak position of elemental Ge is reported at BEs typically between 28.9 and 30.2 eV.^{32–35} BE values up to 3.4 eV higher than the elemental peak position correspond to increasing Ge oxidation states.³⁶ In consequence, spectrum (2) clearly indicates the oxidation of the Ge deposit after evaporation at elevated temperatures on the Pr oxide surface. The Ge oxidation probably occurs by two mechanisms, namely, first by the formation of –Ge–O–Pr– bonding units due to the buildup of the semiconductor/oxide interface and afterwards by the production of –Ge–O–Ge– entities as a consequence of oxygen diffusion from the oxide into the Ge deposit. According to this two component oxidation model, a fitting procedure of spectrum (2) reveals that the Ge 3d peaks of the –Ge–O–Pr– and –Ge–O–Ge– bonding units are centered at 31.8 and 32.6 eV, respectively. The position of the Ge 3d peak of the –Ge–O–Pr– bonds is expected by electronegativity arguments to be located between the positions of elemental and oxidized Ge. The electronegativity of Pr and Ge on the Pauling scale amount to 1.1 and 2.0, respectively, so that the strong electropositive character of Pr produces a higher electron density on Ge at the –Ge–O–Pr– interface in comparison to the –Ge–O–Ge– environment. It is noted that this trend is well established for Si 2p lines of metal silicates with respect to SiO₂ (Ref. 37) and was recently proven to hold also for the very similar Pr silicate systems (–Si–O–Pr– bonds).³⁸ The position of the Ge 3d peak of the –Ge–O–Ge– bonds at 32.6 eV points to the presence of a Ge oxide film, probably with a stoichiometry close to GeO₂.³⁶ After 16 s of Ge deposition [spectrum (3)], the intensity of this –Ge–O–Ge– species grows, resulting in a slight shift of the center of gravity of the total Ge 3d peak towards 32.6 eV. A drastic change in the Ge 3d spectrum is observed in spectrum (4) after 48 s of Ge evaporation. First, as estimated by visual inspection, the total photoemission intensity of the Ge 3d core level significantly drops in passing from spectrum (3) to (4). This result can only be explained by a partial sublimation of Ge during the Ge deposition at the elevated temperature of ~550 °C, probably in form of GeO. This assumption is reasonable because the volatility of GeO at temperatures above 500 °C was demonstrated in oxidation studies of Ge surfaces in the past.^{35,39–41} Second, the peak shape has evolved into two main lines at 30.1 and 31.8 eV. According to the discussion above, the latter Ge 3d peak position is assigned to the –Ge–O–Pr– bonding configuration located at the semiconductor/oxide interface. The Ge 3d peak at 30.1 eV is characteristic of elemental Ge. Further Ge deposition [spectra (5)–(8)] results in a strong increase of the elemental Ge 3d peak intensity, proving the growth of a non-oxidized, elemental Ge layer on the Pr oxide support. Simultaneously, the Ge 3d interface peak component at 31.8 eV is gradually attenuated in passing from spectrum (5) to (7). A complete attenuation is observed in spectrum (7) which

shows an elemental Ge $3d$ photoelectron line at 29.9 eV, achieved after 284 s of Ge deposition. The peak position and shape are in line with the XPS reference curve (8) for a closed Ge(111) layer, obtained after a longer Ge evaporation time.

A similar picture of the Ge growth mechanism results from the analysis of the corresponding O $1s$ spectra summarized in Fig. 4(b). Curve (1) presents the O $1s$ spectrum of the clean PrO_2 (111) surface with the oxygen peak situated at a binding energy of 529 eV. The small shoulder observed on its high BE side probably results from residual Pr hydroxides adsorbed on the surface.⁴² After 8 s of Ge growth [spectrum (2)], the O $1s$ signal intensity of the Pr oxide at 529 eV decreases and two new features at 530.5 and 531.6 eV emerge, giving rise to a rather broad O $1s$ peak structure. In line with the interpretation of the Ge $3d$ signal, the O $1s$ peaks at 530.5 and 531.6 eV are attributed to the formation of an interface layer with $-\text{Ge}-\text{O}-\text{Pr}-$ bonds and Ge oxide with $-\text{Ge}-\text{O}-\text{Ge}-$ entities, respectively. Again, these peak assignments are supported by electronegativity considerations which suggest an increase of the O $1s$ binding energy in passing from highly ionic $-\text{Pr}-\text{O}-\text{Pr}-$ over mixed ionic-covalent $-\text{Ge}-\text{O}-\text{Pr}-$ towards more covalent $-\text{Ge}-\text{O}-\text{Ge}-$ bonding configurations. Spectrum (3) shows the O $1s$ XPS signal after 16 s of Ge deposition. In accordance with the Ge $3d$ peak analysis, the increasing amount of Ge oxides on the sample is reflected in the O $1s$ spectrum (3) by the fact that the Ge oxide O $1s$ peak at 531.6 eV grows in intensity at the expense of the two other components. The attenuation of the O $1s$ signals at 529 eV (PrO_2) and 530.5 eV (Ge/Pr oxide interface) indicates that the Ge oxides are preferentially situated in the top surface region of the Ge deposit. Again, a drastic change is observed in the O $1s$ photoelectron peak shape after a Ge deposition time of 48 s. As the Ge oxide O $1s$ peak intensity at 531.6 eV is strongly diminished, the O $1s$ peak shape is now dominated by the Pr oxide substrate line at 529.3 eV to which the O $1s$ interface peak is locked in form of a shoulder structure at 530.5 eV. This result strengthens the hypothesis previously derived from the Ge $3d$ peak analysis that, at this growth step, the initially formed Ge oxide compounds are converted to volatile GeO which sublimates at 550 °C.^{35,39–41} With further Ge deposition steps [spectra (5)–(7)], the O $1s$ interface oxygen signal at 530.5 eV is completely attenuated by the growing elemental Ge deposit. In contrast, the O $1s$ photoelectron signal of the Pr oxide substrate at 529.4 eV is strongly attenuated but remains weakly visible even after 284 s of Ge deposition [spectrum (7)], as can be explained by the reported Volmer–Weber growth mode of Ge on Pr oxide surfaces.²⁸ The observed shift of the Pr oxide O $1s$ peak from 529 eV [spectrum (1)] to 529.4 eV [spectrum (7)] probably results from a change in the film stoichiometry (from PrO_2 to Pr_2O_3) due to oxygen depletion by the described interaction with Ge. In this context, it is interesting to note that a similar BE increment of the O $1s$ core line has been detected for cerium oxides when stoichiometry changes from CeO_2 to Ce_2O_3 .⁴³ Furthermore, it is noteworthy that the weak feature in curve (7) at 534 eV originates from $\text{L}_3\text{M}_{2,3}\text{M}_{2,3}$ Auger electrons of elemental Ge.³² The O $1s$ XPS spectrum of a closed Ge(111)

layer is reported as reference [curve (8)]. No O $1s$ peak from the Pr oxide support is detected, indicating the uniform coverage of the Ge layer.

Figure 4(c) presents the corresponding Pr $3d_{5/2}$ spectra collected during the Ge deposition process. In general, the Pr $3d_{5/2}$ peak position turns out to be rather insensitive to the interaction between Ge and the valency of the RE atom (tetra-valent in PrO_2 ; trivalent in Pr_2O_3), being situated throughout our study at a constant BE value (main peak: 933.2 eV; satellite: 928.4 eV). Interestingly, the shape of the satellite structure on the low BE side clearly changes as a function of Ge deposition. For the clean PrO_2 (111) surface [spectrum (1)], the sharp satellite structure is well separated from the main peak. Its origin is known to result from final state interaction effects of the Pr $3d$ and $4f$ electron levels with the O $2p$ states, described in detail in the pioneering work of Ogasawara *et al.* within the theoretical frame of the Anderson impurity model.⁴⁴ Certainly, this characteristic final state XPS feature of cubic Pr oxides is very sensitive with respect to any deviation from stoichiometry and structure.⁴² It is therefore not surprising that the shape of the satellite structure is smeared out during the initial nucleation state of Ge on the PrO_2 surface [spectra (2) and (3)]. On the contrary, the shape of the satellite structure recovers in spectrum (4) and its separation from the main peak remains well conserved during further Ge deposition steps [up to spectrum (7)]. This result points to a stoichiometrically sharp interface between the Ge deposit and the dielectric layer, which has meanwhile evolved to cub- Pr_2O_3 . Finally, as for the O $1s$ signal, the Pr $3d_{5/2}$ photoelectron peak is strongly attenuated after 284 s of Ge deposition but still visible. Again, this experimental finding is best explained by the formation of a Ge film which does not completely cover the Pr oxide support.²⁸ Only after a long evaporation time, a closed Ge layer is formed and the Pr $3d_{5/2}$ signal of the Pr oxide is not detected anymore [curve (8)].

In order to summarize the XPS insights, the Ge $3d$, O $1s$, and Pr $3d_{5/2}$ XPS intensities were extracted from the measurements by a fitting procedure (not shown) and the results are plotted versus Ge deposition time in Fig. 5. Figure 5(a) shows the behavior of the signals from the Pr oxide support. When the Ge evaporation starts, both the Pr $3d_{5/2}$ and O $1s$ peaks due to $-\text{Pr}-\text{O}-\text{Pr}-$ bonds get attenuated by the formation of an interface layer and subsequently by GeO_x species growing on top. After 48 s of Ge growth, the intensity trend of the two substrate peaks is inverted and the detected signal strength increases again. As already discussed, this change is explained by the reduction of the overlayer thickness, caused by the sublimation of GeO from the surface. With further deposition steps, a pure Ge deposit grows on the surface, leading to a decrease of the Pr oxide substrate signals.

Figure 5(b) shows the intensity behavior of the Ge $3d$ and O $1s$ signals originating from the semiconductor/oxide interface. The XPS peaks corresponding to the $-\text{Ge}-\text{O}-\text{Pr}-$ bonds arise in the first stage of growth after 8 s when the interfacial layer starts to build up. After 16 s the intensity is slightly attenuated because GeO_x species form on top due to oxygen diffusion from the Pr oxide into the Ge deposit. The $-\text{Ge}-\text{O}-\text{Pr}-$ peak intensity is highest after 48 s, as a conse-

FIG. 5. O 1s ($\blacktriangle$), Pr 3d_{5/2} ($\bullet$), and Ge 3d ($\blacksquare$) intensities vs Ge deposition time for Pr oxide substrate (a), interface (b), Ge oxide (c), and elemental Ge film (d).

quence of GeO sublimation which again partially uncovers the interfacial layer. With further Ge evaporation (56–284 s), the $-\text{Ge}-\text{O}-\text{Pr}-$ bonds are buried under the growing pure Ge deposit, resulting in a complete attenuation of the interface signals.

Figure 5(c) illustrates the formation of oxidized Ge on top of the Ge/Pr oxide interface. GeO_x species show up already after 8 s. After 16 s, an increase at the expense of the $-\text{Ge}-\text{O}-\text{Pr}-$ bonding entities is observed, suggesting that Ge oxide forms on top of the $\text{Ge}-\text{O}-\text{Pr}$ interface. Starting from 48 s, no GeO_x component is detected in the XPS spectra

FIG. 6. He I UPS spectra vs Ge evaporation time.

anymore. This result indicates that Ge oxide has completely sublimated and the Ge deposit grows from this stage onward in elemental form.

Finally, Fig. 5(d) reports the formation of the pure Ge overlayer. The corresponding elemental Ge peak is first observed after 48 s of Ge deposition and increases then continuously as a function of the Ge layer thickness.

D. UPS

Figure 6 reports the He I UPS spectra collected in-situ during the Ge growth on the Pr oxide support.

Curve (1) refers to the clean $\text{PrO}_2(111)$ surface. The main structure observed, a broad band which extends from 2.7 to 7.2 eV, is primarily attributed to the O 2p states of PrO_2 . The bandwidth is in good agreement with both experimental findings by XPS (Ref. 4) and *ab initio* band structure calculations.^{19,45–47} Furthermore, it is noted that this interpretation is in line with the VB characterization of CeO_2 , an isotropic compound with respect to PrO_2 intensively studied in the past for its catalytic and optical properties.^{18,19,47} The additional feature detected in spectrum (1) at 8.3 eV is not reported in the above cited theoretical PrO_2 (and CeO_2) VB studies. It is tentatively assigned to an oxygen vacancy defect band, generated in the process of oxygen depletion. This hypothesis looks reasonable in the light of the above presented XRD data and the well known tendency of PrO_2 to reduce with time to Pr_2O_3 at elevated temperatures in UHV.^{18,19}

After 8 s of Ge evaporation [spectrum (2)], a significant change in the appearance of the VB region is observed, namely, the formation of three bands at 5.5, 8.3, and 11.6 eV. According to the XPS data, this result can be interpreted as the build-up of an interfacial Ge layer with mainly $-\text{Ge}-\text{O}-\text{Pr}-$ bonds on top of PrO_2 .

After further 8 s of Ge deposition [curve (3)], the VB structure is essentially conserved but a shift towards higher

BEs occurs, displacing the maxima of the three bands to 6.1, 9.2, and 13.1 eV. This effect is attributed to the formation of $-\text{Ge}-\text{O}-\text{Ge}-$ entities above the $-\text{Ge}-\text{O}-\text{Pr}-$ interface, because the spectrum resembles the typical VB shape of Ge oxide.^{35,36,48,49} Thus, the lowest peak at 6.1 eV is identified as the lone-pair states of nonbonding O $2p$ electrons of the bridging oxygen atoms that interconnect the Ge oxide network. The second feature at 9.2 eV is the result of partial covalent bonding between Ge $4p$ and O $2p$ orbitals. Finally, the valence band with the highest BE at 13.1 eV is due to Ge $4s-\text{O } 2p$ bonding states.⁵⁰

Spectrum (4) illustrates the status of the sample after 48 s of Ge evaporation. It is known from the XPS study above that, in passing from spectra (3) to (4), a substantial amount of the Ge oxide deposit evaporates, probably in form of volatile GeO. In consequence, a transition state of the Ge film growth on the Pr oxide surface is probed, where uncovered Pr oxide areas ($-\text{Pr}-\text{O}-\text{Pr}-$ bonds), Ge/Pr oxide interface regions ($-\text{Ge}-\text{O}-\text{Pr}-$ bonds), and elemental Ge islands ($-\text{Ge}-\text{Ge}-$ bonds) coexist on the surface and contribute to the He I UPS signal. On the basis of photoionization cross section arguments,¹⁷ the principal feature observed in spectrum (4) at nearly 5 eV is hence attributed to O $2p$ states from Pr oxide and interfacial Ge/Pr oxide domains.

Curves (5)–(7) describe the evolution of the Ge deposit towards a closed layer structure. First, the increase of Ge coverage with deposition time results in the development of Ge $4p$ states on the low BE part of the spectra.^{51,52} The He I UPS signal intensity of Ge $4p$ electrons is weak compared to O $2p$ electrons, because of the lower ionization cross section.¹⁷ The dominant peak in spectra (5)–(7) is therefore assigned to O $2p$ states from uncovered Pr oxide surface regions, an interpretation in line with the residual Pr oxide signals detected above by XPS. Furthermore, in passing from spectra (5) to (7), this peak shifts by about 0.8 eV towards lower BEs, moving to 4.2 eV after 284 s of Ge evaporation. According to the XRD studies presented above, this result can probably be attributed to the changing stoichiometry of the Pr oxide support during the Ge deposition, namely, the reduction of the Pr oxide film from PrO_2 (111) to $\text{cub-Pr}_2\text{O}_3$ (111).

Finally, curve (8) reports as a reference the VB study of a closed epitaxial Ge (111) layer, obtained after a prolonged evaporation time. The spectrum is in agreement with He I UPS data on Ge(111) surfaces reported in the literature.^{35,53} The wide band from 0 to 5 eV shows the contribution of Ge $4p$ states to the VB and the peak at 7.7 eV is the result of hybridized Ge $4p-4s$ states. The pure Ge $4s$ band, expected at around 10 eV from theoretical DOS calculations, is not visible, due to the fact that the He I ionization cross section for these states is by two orders of magnitude lower than for Ge $4p$ electrons.¹⁷

IV. DISCUSSION

The growth of Ge on a Pr oxide/Si(111) support system was studied by a multiple surface science technique approach.

Ex situ XRD and SR-GIXRD were used to characterize

FIG. 7. (Color online) Scheme of the growth mechanism of Ge on the Pr oxide/Si(111) support system. Solid arrows indicate Ge evaporation on the sample surface; dashed arrows account for O diffusion from the Pr oxide to the growing Ge deposit.

the crystallographic structure of the samples *before* and *after* the deposition of Ge. The following epitaxial relationships of Pr oxide with the Si(111) substrate were derived *before* Ge evaporation:

$$\text{Vertical: PrO}_2[111] \parallel \text{Si}[111],$$

$$\text{In plane: PrO}_2\langle -1-12 \rangle \parallel \text{Si}\langle 11-2 \rangle.$$

The type-B epitaxy of PrO_2 is accounted for by the antiparallel notation of the PrO_2 and Si in-plane azimuths.⁸ As already pointed out in the XRD chapter, the actual Pr oxide phase before Ge growth is an oxygen-deficient $\text{PrO}_{2-\delta}$ phase ($0 < \delta < 0.2$) with the typical fluorite crystal structure of PrO_2 . After Ge deposition, PrO_2 has evolved to $\text{cub-Pr}_2\text{O}_3$ by exchanging oxygen atoms with the growing Ge deposit as sketched in Fig. 7. The resulting epitaxial relationships of the Ge/Pr oxide/Si(111) heterostack is given by

$$\text{Vertical: Ge}[111] \parallel \text{cub-Pr}_2\text{O}_3[111] \parallel \text{Si}[111],$$

$$\text{In plane: Ge}\langle 11-2 \rangle \parallel \text{cub-Pr}_2\text{O}_3\langle -1-12 \rangle \parallel \text{Si}\langle 11-2 \rangle.$$

The parallel and antiparallel in-plane alignment of the Ge and $\text{cub-Pr}_2\text{O}_3$ lattices with the Si substrate azimuth, respectively, highlights the type-A/B/A stacking configuration of the $\text{Ge}(111)/\text{cub-Pr}_2\text{O}_3(111)/\text{Si}(111)$ heterostructure. Here, it must be noted that the type-A configuration of Ge was determined by *in situ* RHEED, a result in line with a previous SR-GIXRD study.²⁸

In situ RHEED, XPS, and UPS were applied to shed light on the interaction between the Ge deposit and the Pr oxide support during the initial growth stages. RHEED results are in agreement with the epitaxial relationships obtained by XRD and SR-GIXRD. In addition, RHEED detected the occurrence of an amorphization reaction during the first Ge deposition steps (8 and 16 s). XPS and UPS identified this amorphous layer as $\text{GeO}_{2-\delta}$ and the following growth scenario emerged from the data analysis (Fig. 7). The starting point is the $\text{PrO}_{2-\delta}(111)/\text{Si}(111)$ support system de-

scribed above [Fig. 7(a)]. After 8 s of Ge deposition [solid arrow in Fig. 7(b)], first an interfacial layer with $-\text{Ge}-\text{O}-\text{Pr}-$ bonds is built up. Then, on top of this interface, $-\text{Ge}-\text{O}-\text{Ge}-$ entities start forming as a result of the diffusion of O atoms from the PrO_2 film, unstable at elevated temperatures in UHV, to the Ge deposit [dashed arrow in Fig. 7(b)]. In support of this hypothesis, praseodymium oxide was reported to have the maximum activity in isotopic exchange with molecular oxygen among the RE oxides;^{54,55} furthermore, praseodymia-based solid solutions have been widely investigated in catalysis due to their enhanced oxygen storage capacity and high lattice oxygen mobility, releasing oxygen in a $\text{Pr}^{4+} \rightleftharpoons \text{Pr}^{3+}$ redox process at temperatures above 350 °C.^{56,57} After 16 s of Ge evaporation [Fig. 7(c)], the average oxidation state of Ge increases, as revealed by the shift of the XPS Ge 3d core line towards higher BEs.³⁶ The so formed Ge oxide is probably a substoichiometric Ge dioxide, labeled in the following as $\text{GeO}_{2-\delta}$. Between 16 and 48 s of Ge deposition [Fig. 7(d)], the PrO_2 film completely converts to a cub- Pr_2O_3 phase in consequence of the loss of O atoms diffused towards the Ge deposit. It is interesting to note that the formation of a cubic sesquioxide in the reduction process of PrO_2 is not predicted by theory, according to which the hexagonal phase is favorable.¹⁹ It must, however, be pointed out that these theoretical calculations apply to the zero temperature/pressure limit and that they refer to bulk materials without considering the properties of thin films under heteroepitaxy constraints [indeed, hex- Pr_2O_3 almost perfectly matches Si(111) ($\sim +0.5\%$) but its misfit to Ge ($\sim -3.6\%$) is comparable to the direct mismatch of Ge with respect to Si ($\sim 4.2\%$); on the contrary, cub- Pr_2O_3 represents a more appropriate buffer because its lattice is $\sim 2.7\%$ bigger than two times the Si lattice and $\sim 1.4\%$ smaller than two times the Ge lattice]. At this step, no further O is available anymore in the Pr oxide [as represented by the absence of the dashed arrow in picture 7(d)]. Since the Ge evaporation is continued, the $\text{GeO}_{2-\delta}$ deposit transforms to GeO, which is well known to be volatile in UHV at temperatures above 500 °C.^{35,39–41} The sublimation of GeO uncovers the interfacial layer, on top of which an elemental Ge deposit can now grow, as illustrated in Fig. 7(e) after 48 s of Ge deposition. The spotty RHEED pattern as well as the presence of Pr oxide related XPS O 3d and Pr 3d signals up to 284 s of Ge evaporation confirm the three-dimensional Volmer–Weber growth mode of Ge on Pr_2O_3 .²⁸ The Ge layer thus grows by islands, as depicted in Fig. 7(e). After an extended evaporation time and by suitably tuning the deposition parameters, the growth front of the Ge deposit smoothes out, resulting in the growth of an atomically flat and continuous Ge(111) layer structure on cub- $\text{Pr}_2\text{O}_3(111)/\text{Si}(111)$. At this final stage, both the XPS and UPS spectra are in line with reference data reported in the literature for elemental Ge(111) surfaces.

In conclusion, the interaction between the growing Ge layer and the PrO_2 support system can be divided into two steps. The first one, represented in Fig. 7(c), regards the conversion of PrO_2 to cub- Pr_2O_3 with formation of GeO_2 ,

Then, since Pr_2O_3 does not supply oxygen anymore and Ge is continuously evaporated, GeO_2 transforms to GeO which sublimates,

The reduction of PrO_2 to cub- Pr_2O_3 by Ge deposition is hence summarized by the chemical reaction

whose standard molar enthalpy ΔH^0 is clearly exothermic with a value of -304 KJ/mol (using -1809.9 , -261.9 , and -959.8 KJ/mol as ΔH^0 for Pr_2O_3 ,^{58,59} GeO ,⁶⁰ and PrO_2 ,⁶¹ respectively). At this stage [after 48 s of Ge deposition, Fig. 7(e)] cub- Pr_2O_3 is formed which acts as a thermodynamically stable support for elemental Ge heteroepitaxy.

It is noted in support of this growth scenario that the deposition of CeO_2 dielectrics on Ge substrates was recently reported to show a similar behavior, namely the chemical reduction to Ce_2O_3 in consequence of an interface reaction.⁶²

V. SUMMARY AND OUTLOOK

The initial MBE growth stages of Ge on Pr oxide/Si(111) heterostructures were investigated by *in situ* surface science techniques and *ex situ* diffraction experiments. It was shown that, prior to Ge evaporation, the Pr oxide consists of a type-B PrO_2 lattice with a certain oxygen deficiency. In the first deposition steps, an amorphous Ge oxide layer forms on the sample surface, due to the interaction with the substrate, namely, the diffusion of O atoms from the PrO_2 -like support to the growing semiconductor deposit. When the initial PrO_2 -like phase has been fully reduced by Ge to cub- Pr_2O_3 , no oxidizing species are available anymore in the deposition process and Ge oxide sublimates, probably in form of GeO. The cub- Pr_2O_3 surface acts now as a thermodynamically stable support for the growth of elemental Ge, which occurs according to a Volmer–Weber mode. Finally, after an extended deposition time, a smooth, single crystalline, type-A (111) oriented Ge layer is formed on the type-B cub- $\text{Pr}_2\text{O}_3(111)/\text{Si}(111)$ substrate.

Further analyses by SR-GIXRD techniques are currently ongoing to evaluate the actual extent of O deficiency in the initial PrO_2 -like support. Moreover, an optimization of the Ge deposition parameters, such as temperature and evaporation flow, is in progress to improve the crystalline quality and the flatness of the 100% Ge(111) layer integrated on Si(111) via a cub- $\text{Pr}_2\text{O}_3(111)$ oxide support heterostructure.

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