Epitaxial growth of germanium on silicon using a Gd2O3/Si (111) crystalline template

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This work presents a study of the epitaxial growth of Ge on Si (111) using a Gd$_2$O$_3$ crystalline template. A smooth two-dimensional Ge layers is obtained from the coalescence of initially three-dimensional Ge islands grown in the Volmer–Weber mode. Ge takes its bulk lattice parameter at the very early stages of its growth. A detailed x-ray pole figure analysis reveals that the epitaxial relationship between the layers and the Si substrate is $[1-10]$Ge$(111)\|$ $[-110]$Gd$_2$O$_3(111)\|[1-10]$Si(111) and that microtwins are formed in the Ge layer. © *2010 American Vacuum Society.* [DOI: 10.1116/1.3478301]

I. INTRODUCTION

The integration of a high quality germanium epilayers on Si has motivated numerous researches in the recent years. Due to its high hole mobility, Ge appears as an interesting channel material alternative to Si for high-frequency metal oxide semiconductor field-effect transistor (*p*-MOSFETs). Ge/Si crystalline templates could also be used as templates for the integration of III-V based heterostructures on standard industrial Si wafer, thanks to the negligible lattice mismatch between Ge and GaAs (~0.12%). Fabricating such heterostructures could allow combining high-performance micro- and optoelectronic functionalities on the same silicon basewafer. The direct epitaxy of Ge on Si is challenging: the lattice mismatch between these two materials is about 4.1%, so that threading dislocations are generated in the growing material once the deposited thickness exceeds a critical thickness[1] of a few monolayers. Many strategies have been developed to overcome this difficulty, and several recent studies have demonstrated the opportunity of using crystalline oxides/Si templates such as SrHfO$_3$/Si (001),[2] PrO$_2$/Si (111),[3] SrTiO$_3$/Si (001),[4–6] and Gd$_2$O$_3$/Si (111) (Ref. [7]) for the integration of Ge or III-V materials on silicon. Due to the strong crystallographic and chemical heterogeneity between III-V or IV-IV semiconductors and oxides, the elevated lattice mismatch between these materials is fully accommodated by a network of dislocations, confined at the heterointerface, and formed at the very early stages of the growth. As a consequence, the semiconductor grows with its bulk lattice parameter on the oxide surface and does not contain any threading defect related to any plastic relaxation mechanism, as explained in detail in one of our earlier studies.[8] Schroeder *et al.* extensively studied the Ge/Pr$_2$O$_3$/Si (111) system. They demonstrated that Pr$_2$O$_3$/Si (111) templates could be used for the integration of single crystal two-dimensional Ge layers on Si[3]. Simple geometric considerations indicate that two Ge domains should be formed on the Pr$_2$O$_3$ (111) surface. Schroeder *et al.* showed that electrostatic effects at the heterointerface select one of these two domains, leading to a single domain Ge growth.[9] Furthermore, this group has recently evidenced that microtwins were formed in Ge epilayers grown on Pr$_2$O$_3$/Si (111) templates, due to the fact that these layers result from the coalescence of initially three-dimensional Ge islands.[10]

In this work, we show that Gd$_2$O$_3$/Si (111) epilayers can also be used as templates for the integration of Ge on Si. Gd$_2$O$_3$ has the same bixbyite crystal structure as Pr$_2$O$_3$ but presents some interesting features: Gd is a single valence metal ion (+3), so that Gd$_2$O$_3$ is the single stable Gd oxide, while both Pr$_2$O$_3$ and PrO$_2$ oxides can be formed. Moreover, Gd$_2$O$_3$ is more stable in air than Pr$_2$O$_3$. In the end, Gd$_2$O$_3$/Si (111) templates present a high monocrystalline quality, as recently demonstrated in Ref. [11]. Based on the detailed reflection high energy electron diffraction (RHEED) and x-ray diffraction (XRD) analyses, we show (i) that Ge takes its bulk lattice parameter as soon as the growth begins, thus obeying the specific accommodation mode described in Ref. [8]; (ii) that Ge contains microtwins, the proportion of twinned material being precisely determined.
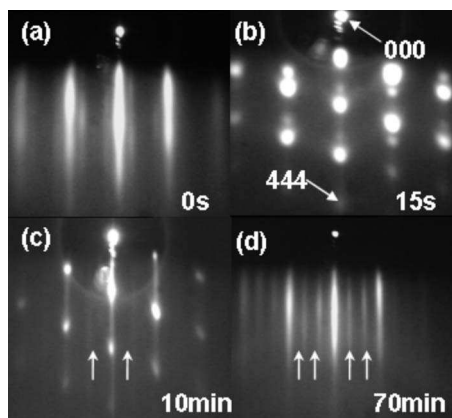
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FIG. 1. Evolution of the RHEED patterns as a function of Ge thickness. The arrows in (c) and (d) highlight the Ge surface reconstructions.

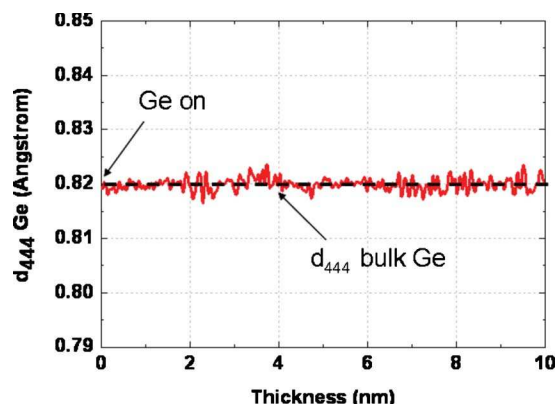
FIG. 2. (Color online) Evolution of the 444 interatomic distance during the early stages of the Ge growth. d_{444} remains constant ($\sim$0.82 Å) and equals to its value of bulk Ge.

II. EXPERIMENT

The sample considered in the following was grown on a nominally (111)-oriented silicon substrate. Before growth, the Si substrate was cleaned using a HF–NH$_4$F solution. The H-terminated substrate was then introduced in the solid-source molecular beam epitaxy chamber (RIBER EVA 32 reactor), and a 6 nm thick (111)-oriented Gd$_2$O$_3$ layer was grown (at 700 °C and under a partial O$_2$ pressure of 10^{-6} Torr, using an electron beam evaporated single crystal Gd$_2$O$_3$ target, as extensively described in Ref. 11). A 280 nm Ge layer was then grown (using a standard Knudsen cell) on this Gd$_2$O$_3$/Si (111) template, at 400 °C and at a growth rate of 4 nm min^{-1}. The sample was characterized *in situ* by RHEED (30 kV e-beam gun) and *ex situ* by XRD (pole figure and rocking curve measurements) using a Panalytical X'Pert Pro diffractometer.

III. RESULTS AND DISCUSSION

A. Accommodation and growth mode

Figure 1 shows the evolution of the RHEED pattern (recorded along one of the Gd$_2$O$_3$ ⟨110⟩ azimuths) during Ge growth. Before Ge growth starts, the Gd$_2$O$_3$ surface [Fig. 1(a)] presents well-defined streaky lines and a clear ×4 reconstruction, indicating the good crystal and surface quality of the oxide template. Once Ge growth begins, the pattern turns spotty [Fig. 1(b)] indicating an initial three-dimensional growth in the Volmer–Weber mode. At this stage of the growth, the RHEED pattern is very similar to that observed in Ref. 3 during the growth of Ge on PrO$_2$/Si (111) templates, or even to that observed during the growth of InP on Gd$_2$O$_3$/Si (111) templates.[7] As explained in Ref. 3, this pattern results from the superimposition of the (111)-oriented Ge Bragg peaks and of the diffraction of uncovered oxide regions. After the deposition of 40 nm of Ge, the RHEED pattern starts exhibiting diffraction lines, indicating that the initially formed Ge islands coalesce to form a two-dimensional layer. In Fig. 1(c), a clear ×2 reconstruction of the Ge surface can be observed. At the end of the growth [Fig. 1(d)], the RHEED pattern presents bright streaky lines

resulting from the diffraction of a flat and well crystallized Ge epilayer. The Ge surface presents a (3×3) reconstruction, already observed for Ge(111) surfaces, possibly with the impurity of carbon or gadolinium.[12] The evolution of the out-of-plane Ge 444 interatomic distance during the early stages of the growth was measured by recording the evolution of distance between the 000 transmitted spot and the 444 Ge reflection spot on the RHEED pattern [as indicated in Fig. 1(b)]. The result is displayed in Fig. 2. The RHEED camera length was calibrated assuming that the Si substrate presents the bulk Si lattice parameter. The Ge 444 interatomic distance remains constant and equals to its value in bulk Ge ($\approx$0.82 Å) during Ge growth. In particular, Ge takes its bulk lattice parameter as soon as it can be measured by RHEED. This behavior has already been observed for several semiconductor/oxide systems.[7,8] For standard mismatched IV-IV or III-V systems, the growing material takes the in-plane lattice parameter of the substrate at the early stages of the growth and undergoes a plastic relaxation process during which it progressively recovers its bulk lattice parameter at the expense of the formation of threading dislocations. In contrast here, Ge takes its bulk lattice parameter as soon as growth begins. The lattice mismatch between Ge and Gd$_2$O$_3$ is fully accommodated by forming interface dislocations confined at the heterointerface, as described in Ref. 7 for the InP/Gd$_2$O$_3$ system or in Ref. 8 for the InP/SrTiO$_3$ system.

B. Epitaxial relationship and evidence for twin formation in the Ge layer

X-ray pole figures were recorded on the sample. For that purpose, the x-ray incident beam was point focused onto a 10 mm^2 area using a polycapillary lens and crossed slits. A Ge 111 pole figure is shown in Fig. 3(a). On this figure, the radial scale corresponds to the polar angle (ψ), while the azimuthal incidence (ϕ) varies along the perimeter. The 2θ angle was fixed at 27.28°, which corresponds to the Ge 111 Bragg angle. Thus, all the visible reflections on the pole figure correspond to the diffraction of planes with interplanar distances close to the Ge {111} planes. The coordinates of
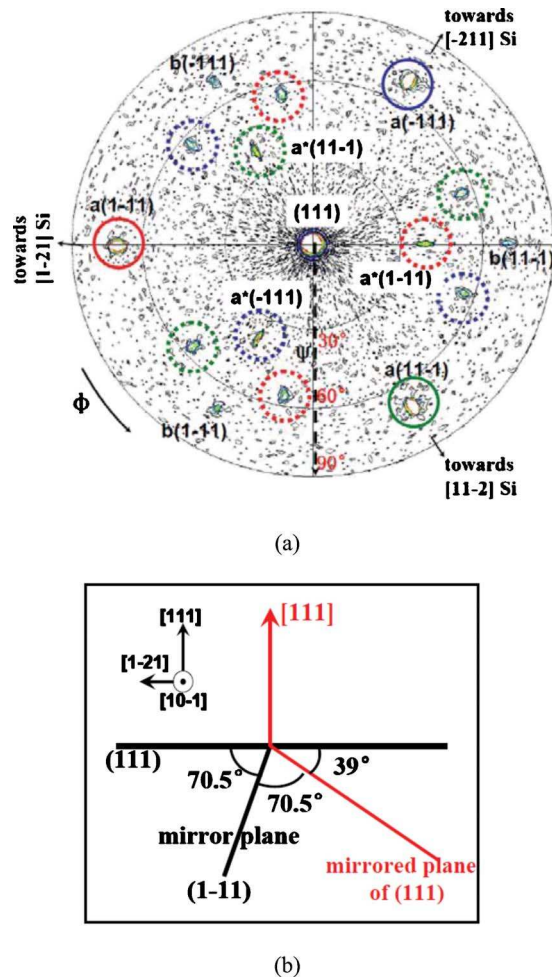
(a)

(b)

FIG. 3. (Color online) (a) X-ray pole figure recorded near the 111 Si reflections on the sample of Ge/Gd$_2$O$_3$/Si (111). (b) Sketch of the twinning sequence for one of the Ge {111} plane family.

FIG. 4. (Color online) Rocking curves corresponding to the spots in the x-ray pole figure in Fig. 3(a).

these reflections allow orientating the different Ge variants with respect to each other in the real space. Additionally, for each reflection in the pole figure of Fig. 3(a), defined by its polar and azimuthal angles, rocking curves where recorded in order to scan the reciprocal space, measure the lattice parameters, and thus detect the different layers of the heterostructure, namely, the Si substrate, the Gd$_2$O$_3$ template, and the Ge layer and determine their relative orientations. Some of these rocking curves are plotted in Fig. 4. Using these rocking curves, the pole figure of Fig. 3(a) has been fully indexed. The spot in the center labeled (111) (symmetric conditions) indicates that Ge is (111)-oriented (same out-of-plane orientation as the Si substrate). The threefold symmetric reflections located at $\psi=70°$ and $\phi=60°$, 180°, and 300° and labeled $a(-111)$, $a(1-11)$, and $a(11-1)$ correspond to the main variant of the Ge crystal, designated as variant a. The other reflections in the pole figure correspond to the presence of twinned Ge variants in the layer. The set of low-intensity threefold symmetric reflections at $\psi=70°$ and $\phi=0°$, 120°, and 240° [labeled $b(-111)$, $b(1-11)$, and $b(11-1)$] indicate the presence of a second Ge variant in the layer (labeled variant b), twisted of 60° around the Ge (111) ver-
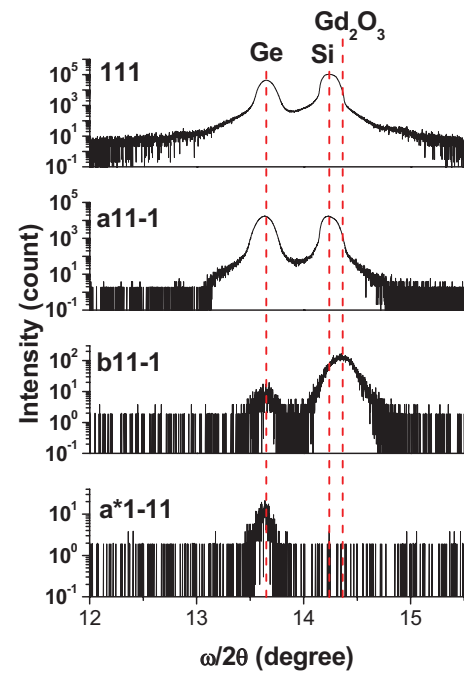
tical direction with respect to variant a. This variant b corresponds to the presence of the twinning with respect to the Ge(111) surface. The mirror planes of these microtwins are the (-111), $(1-11)$, and $(11-1)$ Ge inclined planes, respectively. Simple geometric considerations allow concluding that the other reflections in the pole figure result from the presence of twins in the Ge layer. The reflections marked by red, green, and blue dotted circles correspond to the twinning of the Ge(111) surface plane relatively to the Ge $(1-11)$, $(11-1)$, and (-111) inclined planes, respectively. This twinning sequence is sketched in Fig. 3(b) for the Ge $(1-11)$ plane. On this figure, the trace of the (111) and $(1-11)$ Ge planes are plotted in the $(10-1)$ Ge plane. In this plane, the symmetric of the Ge (111) plane with respect to the trace of the Ge $(1-11)$ planes (mirror plane) is labeled as mirrored plane of (111). It forms an angle of 39° with respect to the Ge (111) planes. These planes, corresponding to the twin of the Ge (111) planes with respect to the Ge $(1-11)$ planes, lead to the observation of a Ge 111 reflection in the pole figure, at $\psi=39°$ and $\phi=0°$. This reflection is marked with a dotted red circle and labeled $a^*(1-11)$ in Fig. 3(a). Similarly, $a^*(11-1)$ and $a^*(-111)$ correspond to the twinning of the Ge(111) surface plane relatively to the $(11-1)$ and (-111) Ge planes. The other secondary reflections located at $\psi=56°$ correspond to the twinning of the Ge $(1-11)$, $(11-1)$, and (-111) inclined plane relatively to each other. Such twins have already been observed by Schroeder *et al.* during the growth of Ge on Pr$_2$O$_3$.[10] Their formation has been interpreted as occurring during the coalescence of the initially formed Ge islands, due to the presence of facets at the surface of these islands.

The ω-2θ rocking curves recorded around the Ge 111, a11−1, b11−1, and a^*1−11 reflections of the pole figure of Fig. 3(a) are plotted in Fig. 4. The rocking curve recorded around the Ge 111 symmetric reflection presents two well resolved peaks centered at ω=13.65° (Ge 111 reflection) and ω=14.25° (Si 111 reflection). This confirms that the Ge layer presents the same (111) out of plane orientation as that of the Si substrate. The rocking curves recorded around the Ge a11−1 reflection also present two peaks corresponding to aGe 111 and aSi 111 reflections, respectively. This indicates that the in-plane orientation of the Ge variant a is the same as that of the Si substrate. The rocking curves recorded around the Ge b11−1 (Ge variant b) presents a significantly different shape: the intensity of the Ge 111 peak is 1700 times smaller than that of variant a. Since all the peaks correspond to reflections with the same 111 structure factor and with the same geometrical angle ψ, the diffracted intensities can be directly compared to quantify the proportion of the two variants. This indicates that 0.06% of the Ge layer is twisted 60° around the (111) vertical direction with respect to the Si substrate. The Si 111 reflection is not detected on this rocking curve, as expected for a single crystalline and single domain substrate. The peak centered at ω=14.38° is a 111 reflection of the Gd₂O₃ layer. The Gd₂O₃ lattice is rotated 60° around the (111) vertical direction with respect to the Si substrate, as already shown in Refs. 11, 13, and 14. In the end, the rocking curve recorded around the secondary a^*1−11 Ge reflection at ψ=36° and 59° only presents aGe 111 reflection, showing that only the Ge crystal is twinned with respect to the {111} asymmetric planes. Since the geometrical angles differ, the quantification of these secondary twinned variants is not possible. Nevertheless, the intensity in these rocking curves is several orders lower than the intensity of the rocking curves collected at ψ=70° for the main variant a. This qualitatively indicates that only a few part of the Ge material is twinned with respect to the {111} asymmetric planes.

The results discussed in this section allow determining the relative orientations of the layers in the Ge/Gd₂O₃/Si heterostructure (Fig. 5). The epitaxial relationship between Ge, Gd₂O₃, and Si can be defined as [1−10]Ge (111)∥[−110]Gd₂O₃ (111)∥[1−10]Si (111). Only 0.06% of the Ge material is twisted around the (111) vertical direction with respect to the main Ge variant, and a very few part of the Ge material is twinned with respect to the asymmetric (111) planes.

IV. CONCLUSION

In conclusion, we have demonstrated that crystalline Gd₂O₃/Si (111) templates could be used for the integration of Ge on silicon. Germanium grows in the Volmer–Weber
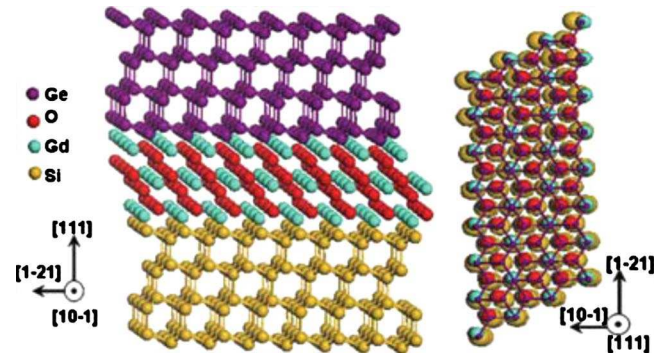

FIG. 5. (Color online) Schematics of the Ge/Gd₂O₃/Si stack, cross-section view (left) and top view (right).

mode and takes its lattice parameter as soon as growth begins, as already observed for several highly dissimilar semiconductor/oxide systems. 0.06% of the Ge material is twisted 60° around the vertical (111) direction, and a few part of the Ge material is twinned with respect to the {111} asymmetric planes. Future work will be focused on the clear identification of the origin of these twins and on the optimization of the Ge growth conditions in order to avoid their formation, thus to develop the quality of the Ge epitaxial film.

ACKNOWLEDGMENTS

[1] R. People and J. C. Bean, Appl. Phys. Lett. **47**, 322 (1985).
[2] J. W. Seo *et al.*, Microelectron. Eng. **84**, 2328 (2007).
[3] A. Giussani *et al.*, J. Appl. Phys. **103**, 084110 (2008).
[4] G. Saint-Girons *et al.*, Appl. Phys. Lett. **92**, 241907 (2008).
[5] G. Saint-Girons *et al.*, Appl. Phys. Lett. **104**, 033509 (2008).
[6] J. Cheng, P. Regreny, L. Largeau, G. Patriarche, O. Mauguin, K. Naji, G. Hollinger, and G. Saint-Girons, J. Cryst. Growth **311**, 1042 (2009).
[7] G. Saint-Girons, P. Regreny, L. Largeau, G. Patriarche, and G. Hollinger, Appl. Phys. Lett. **91**, 241912 (2007).
[8] G. Saint-Girons, J. Cheng, P. Regreny, L. Largeau, G. Patriarche, and G. Hollinger, Phys. Rev. B **80**, 155308 (2009).
[9] T. Schroeder, P. Zaumseil, O. Seifarth, A. Giussani, H.-J. Müssig, P. Storck, D. Geiger, H. Lichte, and J. Dabrowski, New J. Phys. **10**, 113004 (2008).
[10] T. Schroeder, A. Giussani, H. J. Muessig, G. Weidner, I. Costina, Ch. Wenger, M. Lukosius, P. Storck, and P. Zaumseil, Microelectron. Eng. **86**, 1615 (2009).
[11] G. Niu, B. Vilquin, N. Baboux, C. Plossu, L. Becerra, G. Saint-Girons, and G. Hollinger, Microelectron. Eng. **86**, 1700 (2009).
[12] G. Profeta and E. Tosatti, Phys. Rev. Lett. **95**, 206801 (2005).
[13] T. Schroeder *et al.*, J. Appl. Phys. **102**, 034107 (2007).
[14] A. Fissel, D. Kühne, E. Bugiel, and H. J. Osten, Appl. Phys. Lett. **88**, 153105 (2006).