LABORATORY-BASED CHARACTERIZATION OF HETEROEPITAXIAL STRUCTURES: ADVANCED EXPERIMENTS NOT NEEDING SYNCROTRON RADIATION

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ABSTRACT

It is demonstrated that a complex X-ray characterization of semiconductor films epitaxially grown on metal oxide buffer layers and Si(111) substrates is possible using laboratory-based equipment. This is demonstrated with epi-Germanium on Pr$_2$O$_3$ as buffer material. Pole figure measurements prove that epi-Ge layers grow nearly completely single crystalline with exactly the same in-plane orientation (type A) as the Si(111) substrate, while the lattice of the oxide layer is 180° rotated around the [111] surface normal (type B). Only a small fraction (less than 0.6 vol. %) of the epi-Ge exhibits type B rotation twins. The main structural defects are micro twin lamellas lying in {111} planes 70.5° inclined to the wafer surface. The different in-plane orientation of Si substrate and epi-Ge on one side and the Pr$_2$O$_3$ buffer layer on the other side allows a very sensitive analysis of strain and defects even for a 10 nm thick oxide layer buried under some hundred nm of Ge. The epi-Ge layers are nearly fully relaxed and the Pr$_2$O$_3$ buffer layer is compressively strained. Due to the existing defects the Ge (111) netplanes are tilted in a characteristic pattern relative to the Si substrate.

INTRODUCTION

The aim of this contribution is to demonstrate that laboratory-based equipment is able to perform a complex X-ray characterization of heteroepitaxial structures. This is essential for a fast continuous monitoring of deposition processes and for a best possible pre-characterization of selected samples, which may be studied in more detail at a synchrotron. Our subject of interest are epitaxially grown semiconductor – insulator – semiconductor (SIS) structures. Thin metal oxide (Pr$_2$O$_3$, Y$_2$O$_3$, etc.) layers act as buffer between a Si(111) substrate and the top semiconductor layer of Ge, Si, Si$_{1-x}$Ge$_x$, or A$_3$B$_5$ materials. Such structures may be used for new applications in microelectronics (Waser, 2003) or in the case of Ge as a possible template for A$_3$B$_5$ material integration (Sheldon et al., 1985). Besides other techniques like layer transfer, the direct heteroepitaxial growth of SIS structures seems to be a promising way of device preparation (Bojarszuk et al., 2003; Seo et al., 2007). The key problem for this concept of so-called engineered Silicon wafers (Fitzgerald, 2005) is the structural perfection of the semiconductor film. To achieve a sufficient perfection, a complex use of different characterization techniques is required in the development of suited deposition techniques.

Here we focus our interest on epi-Ge/Pr$_2$O$_3$/Si(111) structures and their characterization by X-ray techniques. Due to different lattice constants, heteroepitaxially grown layers are typically biaxially strained. Different crystal structures, diamond-like for Si and Ge on one side and bixbyite for the oxide on the other side, generate the problem of in-plane orientation of the individual layers relative to each other. A combination of different X-ray techniques will be used to solve the follow-
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ing problems: (a) the in-plane orientation of oxide and epi-Ge layer relative to the Si substrate, (b) the strain state of both layers, and (c) the crystal perfection especially of the epi-Ge layer.

EXPERIMENTAL

The investigated SIS structures were deposited in a multi-chamber molecular beam epitaxy (MBE) system on 100mm Si(111) boron doped wafers. To obtain epi-Ge layers of optimized quality, Pr$_2$O$_3$ buffer layers were grown in a multi-step process. It starts with the deposition of hexagonal Pr$_2$O$_3$ on the Si(111) substrate. This layer is transformed by annealing in oxygen to cubic PrO$_2$. In this process, an amorphous Pr silicate layer is formed at the interface of about 2 nm thickness. Regardless of this amorphous layer, the heteroepitaxial relation between substrate and Pr$_2$O$_3$ generated in the deposition process is preserved. The deposition of epi-Ge is done directly on the PrO$_2$ film, which is hereby reduced to cubic Pr$_2$O$_3$ again. The preparation details are described in (Giussani, 2008; Giussani, 2009).

All X-ray measurements were carried out with a Rigaku SmartLab diffractometer using CuK$_\alpha$ radiation in line focus geometry from a 9 kW rotating anode. In the standard XRD arrangement the sample is fixed in a horizontal position and source and detector arm of the diffractometer are moved in a $\Theta$ - $\Theta$ mode. It is possible to rotate the sample around an axis perpendicular to the sample surface (or adjusted to a nearly surface parallel netplane) defined as angle $\Phi$ and to tilt the sample by an angle $\chi$ around an axis defined by the beam direction for $2\Theta = 0^\circ$.

Two different resolution schemes were used depending on the measuring technique. In the low resolution mode (LR), a multilayer X-ray mirror in combination with slit systems is used for beam collimation with or without flat graphite crystal monochromator in front of the scintillation counter. The beam divergence perpendicular to the diffraction plane was modified by the use of different Soller slit systems on source and detector arm. The high resolution mode (HR) uses a twofold Ge (400) crystal behind the X-ray mirror to collimate and monochromatize the X-ray beam.

Pole figure measurements were carried out in low resolution mode without monochromator at a diffraction angle 2$\Theta$ fixed to the desired reflection and performing 360$^\circ$ scans in $\Phi$ at $\chi$ values between 0$^\circ$ and 90$^\circ$. Soller slits with 0.5$^\circ$ divergence acceptance were used on source and detector arm, and the step width for $\Phi$ and $\chi$ of 0.5$^\circ$ was adapted to this. The sample is typically adjusted in such a way that the $\Phi$ axis and the normal of the (111) Si substrate netplanes are parallel.

RESULTS AND DISCUSSION

The first standard activities to characterize a sample are typically X-ray reflectivity (XRR) and X-ray diffraction (XRD) measurements in specular geometry to obtain information about layer thickness, roughness and density and about the off-plane orientation of the oxide and epi-Ge layer. Figures 2 and 3 show typical examples for a sample with 8.5 nm Pr$_2$O$_3$ buffer layer and 82
nm epi-Ge on top. The fitting of the XRR curve with the software RCRefSimW (IHP, 2009) results in a very good agreement between experimental and simulated curve (figure 2). The surface and interface roughness is 0.8 nm and 0.4 nm, respectively. The density of the epi-Ge and the oxide layer is very close to the expected bulk values.

The conventional specular XRD scan (figure 3) shows (111) diffraction peaks of different orders n for the Si substrate (n = 1, 2, 3) and for the Ge layer (n = 1, 3). The broad peak near the forbidden but nevertheless weakly visible Si (222) reflection can be attributed to the Pr$_2$O$_3$ (444) reflection. The 2nd and 6th order of the Pr$_2$O$_3$ (111) reflection is superimposed by the 1st and 3rd order of the (111) reflection of the much thicker Ge layer. The absence of any peak than a (111) reflection confirms that the epi-Ge as well as the Pr$_2$O$_3$ layer have the same (111) off-plane orientation as the Si substrate. The off-plane lattice constant calculated from the Pr$_2$O$_3$ (444) peak position (11.31 Å) is slightly larger than the expected bulk value. This is a first indication for a tetragonal distortion of the Pr$_2$O$_3$ layer. But, this technique gives no information about the in-plane orientation of oxide and epi-Ge layer relative to the substrate.

Pole figure measurement is a well-known technique for texture analysis of polycrystalline materials, which is usually not applied for single crystalline substrates with heteroepitaxial layer on top. But, it turned out that this is a very powerful technique in our case to receive information about the in-plane orientation as well as the structural perfection of the Pr$_2$O$_3$ and epi-Ge layer (Zaumseil and Schroeder, 2008). Figure 4 shows three pole figures of different samples. The pole figure of the blanket Si(111) wafer (figure 4a) exhibits the surface-parallel (111) netplanes in the central spot. Three additional (111) netplanes 70.5° inclined to (111) are visible at Φ = 30° (-111), Φ = 150° (1-11), and Φ = 270° (11-1), respectively. Φ is counted counterclockwise beginning at the top. This pattern demonstrates the threefold symmetry of the [111] direction, which is the result of the stacking sequence of the (111) planes in the diamond-like Si lattice. By definition, this is called a type A stacking sequence. If the cubic oxide and epi-Ge lattice has the same in-plane orientation as the Si substrate, any pole figure measured in a (111) reflection would result in a similar intensity distribution. But, the pole figures of the sample with epi-Ge/Pr$_2$O$_3$ layer stack measured with the Ge (111) reflection shows a different situation (figure 4b).
Besides the same spot pattern characteristic for the Si substrate, there are additional spots visible that are indicating the existence of lattice parts of different orientation. One set of three spots (one of them is marked as O1 in) is exactly 180° rotated relative to the substrate spots. Such a 180° rotation around the [111] wafer normal direction is typical for rotation twins representing a type B stacking sequence of the crystal lattice. Furthermore, there are sets of three times three rod-shaped spots visible (one of them is marked as TA) and an additional set of lower intensity spots 180° rotated (TB). These additional spots in the pole figure are obviously representing structural defects either in the oxide or in the epi-Ge layer.

![Fig. 4: Pole figures of (111) reflections; a) measured at a blanket Si(111) substrate wafer (2θSi = 28.44°), b) epi-Ge/Pr2O3/Si(111) layer stack (2θGe = 27.28°), c) epi-Ge directly grown on Si(111) (2θGe = 27.28°). The intensity covers the range from 1 to 10^7 cps in logarithmic scale. Spots marked in (b) will be analyzed in more detail.](image1)

The pole figure shown in figure 4c demonstrates that an epitaxial growth of Ge directly on Si(111) results in less structural perfection of the epi-Ge layer. It demonstrates that the concept of growing epi-Ge on suitable oxide buffer layers seems to be a promising way to obtain acceptable quality for technological application.

![Fig. 5: θ/2θ XRD scans measured in the spots G0, G1, O1, TA, and TB of the pole figure shown in figure 4b. The vertical lines mark the positions of the Si (111), Ge (111), and Pr2O3 (222) reflection. G0 and G1 is measured in HR mode the others in LR mode.](image2)

For a better understanding of the additional features in figure 4b, XRD scans and reciprocal space maps (RSM) were measured in selected spots. The main conclusions can be drawn from XRD curves summarized in figure 5. Spot G1 shows the (-111) Si and the (-111) Ge reflection only. This indicates that (at least the main part of) the epi-Ge has the same type A orientation as the Si substrate. The Pr2O3 (-222) reflection, which has nearly the same Bragg angle as the Ge (-111) reflection, is visible in spot O1 only. Consequently, the oxide layer is completely of type B orient-
tation. But, spot O1 shows an additional weak peak at the position of the Ge reflection. This results from a small fraction (0.6% in this case) of type B orientation in the epi-Ge layer. The distribution of these type B twins in the epi-Ge layer can be concluded from the ratio between the type B and type A volume in samples with different layer thickness. This ratio decreases with increasing layer thickness, which can be only explained by a preferred location of type B twins near the oxide/Ge interface.

The XRD scans of spot TA and TB in figure 5 indicate a Ge reflection only. Therefore, the origin of these spots must be the epi-Ge layer, where significant fractions of the crystal volume must have a different but well-defined orientation. The pole figure spot TA (and TB) is 39° inclined to G0. The corresponding defect is well-known and usually called microtwin. It’s the result of a similar 180° rotation twinning as for the type B twins but now the rotation axis is one of the [-111], [1-11], or [11-1] directions 70.5° tilted relative to the [111] wafer normal. The cross-section TEM micrograph in figure 6a shows such a defect. Different than typical stacking faults that can also be found in the films, the lamella has a thickness of several atomic layers. Consequently, it is a real volume defect that results in additional {111} planes spots in a pole figure. The microtwins start from the oxide/epi-Ge interface and can reach through the whole layer of type A orientation to the surface. The spots TB are caused by microtwins in Ge grains of type B orientation. Figure 6b shows a TEM plane view of the top layer of a 1 μm thick epi-Ge film.

Type B rotation twins and inclined microtwins are unambiguously detected as observed in pole figure measurements. The microtwins may also contribute to special features of reciprocal space mappings as demonstrated in figure 7, but the pronounced streaks can also be explained by simple stacking faults lying in inclined {111} planes. The RSM shows the Si and Ge (111) reciprocal lattice points. The Ge reflection has a wide halo of diffuse scattering with two streaks. The stronger one points exactly in the [11-1] direction perpendicular to the (11-1) plane, which includes microtwins and simple stacking faults. The second streak points in the [100] direction. It is most likely that this streak is caused by a superposition and projection of
streaks in [-111] and [1-11] direction into the plane of diffraction. It can be suppressed by reducing the beam divergence perpendicular to the diffraction plane with Soller slits of lower angular acceptance. As a result of annealing experiments we found that the RSM streaks change while the volume fraction of microtwins obtained from pole figure measurements remains constant. This is a clear indication for the existence and possible modification of stacking faults.

The free positioning of our sample in \( \Phi, \chi \) and 2\( \Theta \) offers another very interesting possibility to learn more about the detected microtwins. Figure 8 shows a 2\( \Theta \) - \( \chi \) mapping measured along two lines in the pole figure with \( \Phi = 90^\circ \) and \( \Phi = 30^\circ \). The Si and Ge (111) reflections are visible at \( \chi = 0^\circ \). The O1 spot with the Pr\(_2\)O\(_3\) (22-2) and the type B Ge (11-1) and the G\(_1\) spot with Si and type A Ge (-111) reflection are visible at \( \chi = 70.5^\circ \) in the left and right part, respectively. At \( \chi = 39^\circ \), the T\(_A\) and T\(_B\) spots can be found, but they are no isolated spots at \( \chi = 39^\circ \) and 2\( \Theta = 27.28^\circ \). Rather, the peak shape is characterized by a curved streak starting from the Ge (111) reflection and going far beyond the Si (111) reflection at \( \chi > 45^\circ \). This indicates that there exists a more or less smooth transition in the lattice orientation from the Ge matrix to the microtwin as seen in 6a should be considered. They are limited in length and defects of different orientation touch each other (see figure 6b). This is all connected with stress, and the integral result is seen in figure 8.

So far the discussion of structural defects was related to the epi-Ge layer only. The question arises, whether it is also possible to get some information about the structural perfection of the Pr\(_2\)O\(_3\) layer. Due to the different in-plane orientation of Si substrate and epi-Ge on one side and the oxide layer on the other side it is possible to find oxide diffraction spots that are apart from the very small fraction of type B Ge free of any other influence. Figure 9 shows the reciprocal space map of the Pr\(_2\)O\(_3\) (22-2) reflection. The Pr\(_2\)O\(_3\) layer of this sample is 8.0 nm thick and buried under...
133 nm epi-Ge. Even here it is possible to see streaks of increased diffuse scattering that are definitely related to the Pr$_2$O$_3$ peak and not to the weaker type B Ge reflection. The streak directions can again be explained as projections of different $<1\bar{1}1>$ directions into the plane of diffraction, which indicates that inclined (111) planes are also for the oxide preferred locations of structural defects. In fact, this measurement represents the limit for laboratory-based technique. The measuring time was about 60 hours. Synchrotron measurements are absolutely required for further characterization of such thin layers.

The main structural features of the investigated epi-Ge/Pr$_2$O$_3$/Si(111) layer stack discussed above are summarized in figure 10. It shows a stacking sensitive cut through the crystal lattice in a plane given by the [111] and [11-2] direction. Oxide and epi-Ge layer have the same [111] orientation perpendicular to the surface as the Si substrate. The stacking sequence of the Si substrate and the majority of the epi-Ge layer is of type A. A small part of the epi-Ge and the whole oxide layer show a type B stacking. The major type of structural defects in the type A and type B grains of the epi-Ge layer are microtwins (shown for type A only). The (111) lattice planes inside the thin lamella are 39° inclined to the corresponding planes of the matrix, which generates the $T_A$ spot. From TEM studies we know that the microtwins have a thickness of up to 10 atomic layers. The bold line parallel to the microtwin in the epi-Ge layer indicates the existence of stacking faults. Similar structural defects exist in the thin Pr$_2$O$_3$ layer.

The existence of different stacking types in one stack of heteroepitaxial layers opens completely new possibilities to analyze the lattice parameters of individual layers or parts of one layer. In figures 4 and 5 was demonstrated that diffraction spots of type A and B lattices occur at different positions in the pole figure and can thus be analyzed without any superposition. The same situation exists with only few exceptions for all reflections. Thus it is possible to measure the netplane distance of type A and B reflections independently by $\Theta/2\Theta$ scans at well-

**Fig. 10**: Sketch of the main structural features of the investigated epi-Ge/Pr$_2$O$_3$/Si(111) layer stack.

**Fig. 11**: Measured lattice constants of Si, Ge and Pr$_2$O$_3$ vs. $\cos^2\chi$ (top), and a more detailed analysis of the Ge reflections (bottom). For better comparison, the lattice constant of Pr$_2$O$_3$ is divided by 2.
defined diffractometer parameters Φ and χ. The strain state of the oxide and epi-Ge layer can be analyzed by a technique described by (Zaumseil, 2008), where a theoretical cubic lattice constant calculated from the peak position of different inclined reflections is plotted vs. cosine square of the tilt angle χ. The resulting straight line gives the in-plane lattice constant at cos²χ = 0 and the off-plane lattice constant at cos²χ = 1. This technique is comparable to the sin²Ψ method to measure the strain in poly crystalline samples, but here different Bragg reflections under various tilt angles are used. Figure 11 shows the results of such an analysis for a sample with 180 nm epi-Ge on an 8.5 nm thick Pr₂O₃ buffer layer in the as-grown state and after annealing at 825°C for 30 minutes in UHV.

The off-plane lattice constant of the as-grown oxide layer (11.288 Å) is distinctly larger than the in-plane lattice constant (10.989 Å), which indicates that this layer is compressively strained. The annealing procedure has no significant influence on the oxide strain. A more detailed analysis of the epi-Ge layer in figure 11b is surprising at first view. Growing a not fully relaxed material on a substrate with smaller in-plane lattice constant results typically in compressive strain. The observed tensile strain can be explained under the assumption of full relaxation by the difference in the linear coefficients of thermal expansion of Si substrate and epi-Ge layer acting during the cooling from Ge growth (550°C) down to room temperature (Hartmann et al., 2008). This effect is increased by annealing at higher temperature (825°C).

Finally we analyzed the tilt of the (111) netplanes of epi-Ge and Si substrate relative to the wafer surface and to each other. To do this, the sample was adjusted with the surface normal parallel to the Φ axis. The tilt of the (111) netplanes relative to the surface was measured as a function of Φ. It is calculated as the difference between the peak position of a Θ scan carried out at a fixed 2Θ position of the corresponding Bragg peak and one half of this 2Θ value.

Results are shown in the upper part of Figure 12. Fitting with the expected sinus function results in a tilt of 0.33° for the Si substrate (a typical value for production wafers) and 0.13° for the epi-Ge layer. The netplane tilt relative to the surface is obviously reduced by the oxide layer and the following epi-Ge layer. This effect is well-known for strained epi layers on miscut substrates. For relaxed layers it is explained by the preference of the slip system in the direction of the miscut over the other (Nagai, 1974; Riesz et al., 1991; Hess et al., 1999). The lower part of figure 12 shows the tilt of the epi-Ge relative to the Si substrate. It is obvious that there exists a periodic modulation between the measuring points and the fitted sinusoidal function. The differential curve can be fitted again with a sinusoidal curve but now with a periodicity of 120° and amplitude of 0.017°. The maxima correlate to the in-plane directions that
agree with the projection of the directions normal to the tilted and microtwin containing (111) planes into the wafer plane. This shows that the threefold symmetry of the defect generation favored in the inclined (111) planes also has an influence on the flatness of the nearly surface parallel (111) netplanes.

**SUMMARY AND OUTLOOK**

It was shown that a complex characterization of heteroepitaxial semiconductor - insulator - semiconductor structures is possible by a combination of different laboratory-based X-ray techniques. This was demonstrated for epi-Ge/Pr$_2$O$_3$/Si(111) layer stacks. Especially the combination of X-ray pole figure measurements with reciprocal space mapping and high resolution $\Theta/2\Theta$ scans at selected inclined netplanes can be used successfully to determine the in-plane lattice orientation of the layers relative to the substrate, the strain state of all layers, and the structural perfection of epi-Ge and oxide buffer layer.

It was demonstrated that the main part of the epi-Ge layer has the same type A stacking orientation as the Si substrate, but about 0.6% is of type B. The Pr$_2$O$_3$ buffer layer exhibits type B only. The oxide layer is tetragonal distorted due to compressive stress, while the epi-Ge layer is fully relaxed and shows a weak tensile strain explained by the action of different linear coefficients of thermal expansion of Si substrate and epi-Ge layer during cooling down from deposition to room temperature. Furthermore, it was found that microtwins lying in inclined {111} planes are the dominating structural defects in the epi-Ge layer. They generate a characteristic scattering pattern in reciprocal space maps, but the unambiguous identification was done by pole figure measurements. It was found that the tilt of (111) planes relative to the wafer surface decreases from Si substrate to epi-Ge layer, where the well-defined defect orientation causes a periodic in-plane variation of the mean (111) layer plane tilt.

This contribution was mainly focused on the methodical aspects of the X-ray characterization of SIS structures and not primarily on material features. The use of laboratory based equipment offers the possibility of a fast and near-preparation analysis of samples required for an improvement and optimization of the deposition process. Besides the discussed epi-Ge/Pr$_2$O$_3$/Si(111) layer stacks, this methodology was successfully used for the characterization of epi-Si/Y$_2$O$_3$/Pr$_2$O$_3$/Si(111) (Zaumseil *et al.*, 2009), lattice matched epi-Si/Y$_{2-x}$Pr$_x$O$_3$/Si(111) and other heteroepitaxial systems. The density of structural defects in the top semiconductor layer is in the order of $10^9$ cm$^{-2}$, which is definitely too high for microelectronics applications. It was found that post-deposition annealing is able to improve the layer perfection, but the most promising way for a significant defect reduction seems to be a further optimization of the deposition conditions.

Using the described techniques a complex pre-characterization of samples is possible that will be studied in more detail by synchrotron measurements. For example, the position of rotation twins at the oxide/epi-Ge interface was concluded in a rather indirect way from samples of different epi-Ge layer thickness. This was proved for epi-Si on Y$_2$O$_3$/Pr$_2$O$_3$ buffer in a more direct way by synchrotron radiation grazing incidence diffraction measurements under different incident angles (Schroeder *et al.*, 2008). Furthermore, synchrotron radiation measurements are in progress to study the diffuse scattering of structural defects in the top semiconductor and the oxide buffer layer to learn more about the fundamental aspects of defect generation and interaction in such structures.
REFERENCES


