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Sublimation growth of thick freestanding 3C-SiC using CVD-templates on silicon as seeds

P. Hens^{1,2*}, V. Jokubavicius¹, R. Liljedahl¹, G. Wagner³, R. Yakimova¹, P. Wellmann², M. Syväjärvi¹

¹ *Department of Physics, Chemistry and Biology, Linköping University, S-58183 Linköping, Sweden*

² *Materials for Electronics and Energy Technology, University Erlangen-Nuremberg, Martensstrasse 7, D-91058 Erlangen, Germany*

³ *Leibniz Institute for Crystal Growth, Max-Born-Strasse 2, D-12489 Berlin, Germany*

**Corresponding author: phihe@ifm.liu.se, Tel. +46/72/9337696, Fax. +46/13/142337*

Abstract: Cubic silicon carbide is a promising material for medium power electronics operating at high frequencies and for the subsequent growth of gallium nitride for more efficient light emitting diodes. We present a new approach to produce freestanding cubic silicon carbide (3C-SiC) with the ability to obtain good crystalline quality regarding increased domain size and reduced defect density. This would pave the way to achieve substrates of 3C-SiC so that the applications of cubic silicon carbide material having selectively (111) or (001) oriented surfaces can be explored. Our method is based on the combination of the chemical vapor deposition method and the fast sublimation growth process. Thin layers of cubic silicon carbide grown heteroepitaxially on silicon substrates are for the first time used for a subsequent sublimation growth step to increase layer thicknesses. We have been able to realize growth of freestanding (001) oriented 3C-SiC substrates using growth rates around 120 $\mu\text{m}/\text{h}$ and diameters of more than ten millimeters. The structural quality from XRD rocking curve measurements of (001) oriented layers shows good FWHM values down to 78 arcsec measured over an area of $1 \times 2 \text{ mm}^2$, which is a quality improvement of 2-3 times compared with other methods like CVD.

Keywords:

Crystal growth; Defects; Physical vapour deposition; Semiconductors; Epitaxial growth; Thick films

1. Introduction

Different techniques have been reported for production of cubic silicon carbide. Besides the semi-bulk growth by continuous feed physical vapor transport (CF-PVT) [1], methods like the fast sublimation growth process [2, 3] and the vapor-liquid-solid mechanism (VLS) [4] rely on the use of comparatively expensive substrates of hexagonal silicon carbide (4H-SiC or 6H-SiC). In the fast sublimation growth process (FSGP), homoepitaxial growth of hexagonal SiC has shown a structural improvement compared with the substrate [5] while in heteroepitaxy a full polytype conversion to 3C-SiC is still to be mastered [3], and in VLS the growth rate is low. To overcome these problems a two step process for homoepitaxial growth of 3C-SiC by sublimation [3] or by chemical vapor deposition (CVD) [6] was presented on seed layers produced by the VLS technique on hexagonal substrates. Chemical vapor deposition of 3C-SiC on silicon substrates is widely applied to reduce costs [7]. However, it still suffers from a high density of defects due to the large mismatch in lattice parameters and thermal expansion coefficients.

As a new and promising approach for the production of less costly substrates, we present a combination of the FSGP process on 3C-SiC templates produced by CVD on silicon substrates [8]. This new concept combines the use of a low-cost substrate like silicon with the high growth rate and good crystal quality as obtained by FSGP. In addition, it allows to explore (001) oriented cubic SiC surfaces as needed for further heteroepitaxial growth of other cubic semiconductors. For example, the growth of cubic gallium nitride would be very beneficial to explore the more efficient white light emitting diodes due to less influence of the droop effect [9, 10].

2. Material and methods

Our new approach uses a solid polycrystalline source and the CVD-grown (001) oriented 3C-SiC template on on-axis and 3.3° off-axis silicon as the substrate. The 3C-SiC layer thicknesses were between 5 μm and 10 μm on the template. Both types were implemented into a standard FSGP setup with an inductively heated graphite crucible [11]. In this, a spacer with the thickness of one millimeter is applied to create a short source (at bottom) to seed (at top) distance. The spacer opening has typically been 6 mm in diameter for our experiments. A special shape of this spacer with a cone-like opening suppressed the sticking of the grown layer to the applied graphite top-plate and prevented a drop of the grown material into the cavity. In vacuum at a base pressure of 10^{-5} mbar the system realizes a fast species transport from

source to seed driven by a temperature gradient. This FSGP technology provides a combination of high growth rate and crystal quality improvement as has been shown before in homoepitaxial growth of different hexagonal polytypes [5].

To avoid a damage of the thin 3C-SiC layer by the silicon melt, which is formed at temperatures below the typical process temperatures around 1725°C, we placed an additional thin graphite top-plate, which has a certain open porosity, onto the stack. The silicon melt then infiltrates into the pores and forms polycrystalline silicon carbide. By that the melt is removed and no longer endangers the stability of the 3C-SiC template layer, which has become a freestanding seed without any need of pre-growth silicon removal.

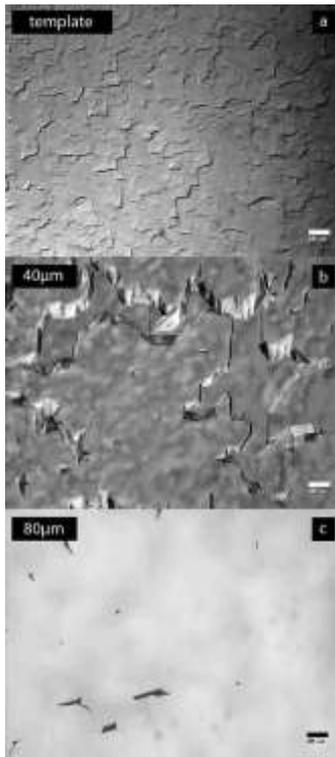
The samples in this work have been produced with a growth rate of about 120 $\mu\text{m}/\text{h}$ compared to growth rates of 10 $\mu\text{m}/\text{h}$ and below as typical for CVD growth systems [7]. Thereby the approach makes it more suitable for bulk-like growth of 3C-SiC for substrate applications.

The system was heated up into the measurement range of the pyrometer under power controlled conditions. The ramp from 1200°C to the growth temperature at 1725°C was performed under temperature control with ramp speeds of either 5 K/min or 20 K/min which influences the initial growth [12]. The system was then kept at the constant growth temperature for times of 20 minutes or 40 minutes after which it was cooled down back to room temperature.

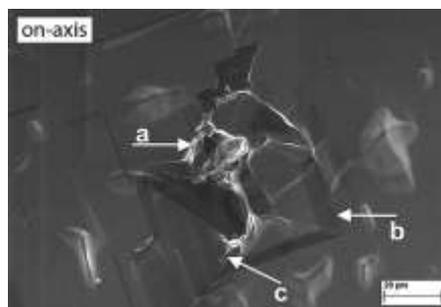
Different characterization techniques were applied like optical microscopy with Nomarski interference contrast, scanning electron microscopy (SEM) in cross section and surface view as well as high resolution XRD Rocking scans on the (002) reflection of cubic silicon carbide.

3. Results

After a growth time of 20 minutes a thickness of 40 μm was reached on on-axis templates representing a growth rate of 120 $\mu\text{m}/\text{h}$. On these samples we could observe a significant increase of the anti-phase domain size, from 10 μm - 20 μm on the CVD-grown templates to 100 μm – 150 μm , in optical microscopy (Fig 1a and b). In this case, where a slow ramp-up speed of 5 K/min was applied, only a small number of planar defects and inclusions could be found within the domains using optical microscopy.

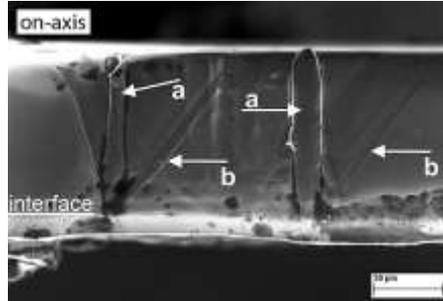


A growth time of 40 minutes resulted in a layer thickness of about 80 μm. These two cases with different growth time prove that the process is stable with a continuous growth speed of 120 μm/h. The process was successfully demonstrated for sample diameters of up to 12 mm, whereas a freestanding layer in the size of a quarter of a 2 inch wafer cracked during cooling down due to stress caused by different thermal expansion coefficients of silicon carbide and the surrounding graphite crucible parts. On these thicker samples no domain boundaries were visible in optical microscopy. In certain areas also the density of other macro-defects like stacking faults, twins and inclusions seems to be very low (Fig 1c). Other areas on the same sample, in particular when using a ramp speed of 20 K/min, showed a rather high density of macro defects as shown in Fig 2, resulting in an inhomogeneous sample quality.

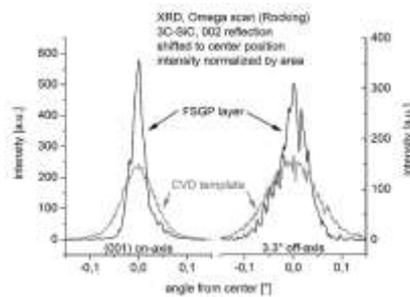


In SEM cross section images many of the defects like inclusions and stacking faults were found to originate at distinctive spots at the interface between the template and the sublimation grown material

(Fig 3). It is very likely that silicon droplets, which had formed on the surface during heat-up, are responsible for these defects, as a comparative growth performed on a template with a wet-chemically removed silicon substrate showed a visibly reduced amount of these defects in optical microscopy.



The improvements in structural quality, as clearly seen in optical microscopy, were verified by high resolution XRD in Rocking mode using the (002) reflection of cubic silicon carbide measured at a large area ($1 \times 2 \text{ mm}^2$) which reflects the overall macroscopic quality. On the low-defect-density areas, like shown in Fig 1c, a significant qualitative improvement was found, assessed from the FWHM value reduction from 253 arcsec for the template to 78 arcsec for the FSGP layer (Fig 4 left). In the defect rich areas discussed above the FWHM value for the grown layer was higher than for the template proving the increased density of large area defects. In general, the values were substantially smaller.



Even when using templates of 3.3° off-axis material a successful growth was found to be possible. No improvement in domain increase was visible in this case in optical microscopy as already the template revealed no clear domain structure. The density of structural defects – as visible in optical microscopy – seems to be very low on these samples compared to the growth on on-axis templates. Despite these promising observations the rocking measurements revealed a variety of domains still to be present in the sample after $90 \mu\text{m}$ of growth (Fig 4 right). The improvement of the FWHM value from 252 arcsec to 195 arcsec for these samples was visible but smaller compared to the samples on on-axis templates.

4. Discussion

The difference in overall structural improvement can probably be explained by two slightly different growth modes. Whereas the off-axis material seems to grow by a large area step-flow mechanism reproducing its structure including defects like the domain boundaries, the on-axis material forms facets. Between the (001) facets acting as the main surface of the materials, facets with orientations like (011) and (111) are formed at the border of two domains when they have a slightly different height. These angled facets are then able to move along the surface of the growing material resulting in an enlargement of several domains at the costs of others. This process cannot be obtained on samples with a sufficient off-axis angle since at that stage the single step-flow mechanism may take place.

5. Conclusions

We have been able to demonstrate the growth of freestanding (001) oriented 3C-SiC samples in the thickness range of 20 μm to 90 μm and diameters of more than ten millimeters. This was realized for the first time by growth using FSGP on templates of cubic silicon carbide on silicon produced by CVD. Structural investigation by XRD rocking curve measurements show a good crystalline quality with FWHM values for the (002) reflection of down to 78 arcsec measured on a footprint of 1x2 mm^2 . The initial growth seems to be a key to maintain the high quality in larger areas. Samples of larger diameters may be obtained by further improvement of the growth system and parameter setup.

Acknowledgements

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References

- 1 Chaussende D, Ferro G, Gourbeyre C, LeBerre M, Barbier D, Monteil Y, Nucleation and Growth of 3C-SiC Single Crystals from the Vapor Phase. *Mater. Sci. Forum* 615-617, 31 (2009)
- 2 Syväjärvi M & Yakimova R, chapter in *encyclopedia – the Comprehensive Semiconductor Science & Technology (SEST)*, Bhattacharya P, Fornari R and Kamimura H (Editors), Elsevier, ISBN 978-0-444-53144-5, Heidelberg, 2011

- 3 Vasiliauskas R, Marinova M, Syväjärvi M, Mantzari A, Andreadou A, Lorenzzi J, et.al., Sublimation Growth and Structural Characterization of 3C-SiC on Hexagonal and Cubic SiC Seeds. *Mater. Sci. Forum* 645-648, 175 (2010)
- 4 Soueidan M, Kim-Hak O, Ferro G, Chaudouet P, Chaussande D, Nsouli B, et.al., How to Grow 3C-SiC Single Domain on α -SiC(0001) by Vapor-Liquid-Solid Mechanism. *Mater. Sci. Forum* 556-557, 187 (2007)
- 5 Syväjärvi M, Yakimova R, Jacobsson H, Janzén E, Structural improvement in sublimation epitaxy of 4H-SiC. *Journal of Applied Physics* 88(3), 1407 (2000)
- 6 Lorenzzi J, Esteve R, Jegenyés N, Reshanov S A, Schöner A, Ferro G, 3C-SiC MOS based devices: from material growth to device characterization. *Mater. Sci. Forum* 679-680, 433 (2011)
- 7 Zielinski M, Portrail M, Chassagne T, Juillaguet S, Peyre H, Nitrogen doping of 3C-SiC thin films grown by CVD in a resistively heated horizontal hot-wall reactor. *Journal of Crystal Growth* 310, 3174 (2008)
- 8 Wagner G, Schwarzkopf J, Schmidbauer M, Fornari R, Influence of Growth Parameters on the Residual Strain in 3C-SiC Epitaxial Layers on (001) Silicon. *Mater. Sci. Forum* 600-603, 223 (2009)
- 9 Kim M-H, Schubert M F, Dai Q, Kim J K, Schubert E F, Piprek J, et.al., Origin of efficiency droop in GaN-based light-emitting diodes. *Appl. Phys. Lett.* 91, 183507 (2007)
- 10 Zhao Y, Tanaka S, Pan C-C, Fujito K, Feezell D, Speck J S, et.al., High-Power Blue-Violet Semipolar (2021) InGaN/GaN Light-Emitting Diodes with Low Efficiency Droop at 200 A/cm². *Applied Physics Express* 4, 082104 (2011)
- 11 Syväjärvi M, Yakimova R, Tuominen M, Kakanakova-Georgieva A, MacMillan M F, Henry A, et.al., Growth of 6H and 4H-SiC by sublimation epitaxy. *Journal of Crystal Growth* 197, 155 (1999)
- 12 Syväjärvi M, Sritirawisarn N, Yakimova R, Initial Growth in 3C-SiC Sublimation Epitaxy on 6H-SiC. *Mater. Sci. Forum* 556-557, 195 (2007)

Figure captions:

Fig 1: Domain size increase: Optical micrographs showing the increase in domain size between (a) the template, (b) a 40 μm layer and (c) a 80 μm layer. All samples are on-axis (001) oriented, scale bars represent 20 μm .

Fig 2: SEM planview: SEM micrograph showing different macro defects found on the surface of the sublimation grown layers like (a) inclusion, (b) planar defects and (c) cracks.

Fig 3: SEM cross section: This image is showing the origin of (a) inclusions and (b) planar defects to be located at the interface. These are likely to be caused by silicon droplets on the template surface.

Fig 4: XRD analysis: HR-XRD Rocking scans of on-axis (80 μm thick) and 3.3° off-axis (90 μm thick) sublimation grown freestanding material compared to the respective CVD-grown templates.