Single Domain 3C-SiC Growth on Off-Oriented 4H-SiC Substrates

Valdas Jokubavicius, Gholam Reza Yazdi, Rickard Liljedahl, Ivan Gueorguiev Ivanov, Jianwu Sun, Xinyu Liu, Schuh Philipp, Martin Wilhelm, Peter Wellmann, Rositsa Yakimova and Mikael Syväjärvi

Linköping University Post Print

N.B.: When citing this work, cite the original article.

Original Publication:

Valdas Jokubavicius, Gholam Reza Yazdi, Rickard Liljedahl, Ivan Gueorguiev Ivanov, Jianwu Sun, Xinyu Liu, Schuh Philipp, Martin Wilhelm, Peter Wellmann, Rositsa Yakimova and Mikael Syväjärvi, Single Domain 3C-SiC Growth on Off-Oriented 4H-SiC Substrates, 2015, Crystal Growth & Design, (15), 6, 2940-2947.

<http://dx.doi.org/10.1021/acs.cgd.5b00368>

Copyright: American Chemical Society

<http://pubs.acs.org/>

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-118525>

Single domain 3C-SiC growth on off-oriented 4H-SiC substrates

Valdas Jokubavicius*,¹, G. Reza Yazdi¹, Rickard Liljedahl¹, Ivan G. Ivanov¹, Jianwu Sun¹, Xinyu Liu¹, Philipp Schuh², Martin Wilhelm², Peter Wellmann², Rositsa Yakimova¹, Mikael Syväjärvi¹

¹Department of Physics, Chemistry and Biology (IFM), Semiconductor Materials Division, Linköping University, 581 83 Linköping, Sweden

²Materials Department 6 (i-meet), Crystal Growth Lab, University of Erlangen, Martens Straße 7, D-91058 Erlangen, Germany

ABSTRACT We investigated the formation of structural defects in thick (~ 1mm) 3C-SiC layers grown on off-oriented 4H-SiC substrates via lateral enlargement mechanism using different growth conditions. A two-step growth process based on this technique was developed, which provides a trade-off between the growth rate and the number of defects in the 3C-SiC layers. Moreover, we demonstrated that the two-step growth process combined with geometrically controlled lateral enlargement mechanism allows formation of single 3C-SiC domain which enlarges and completely covers the substrate surface. High crystalline quality of the grown 3C-SiC layers is confirmed using high resolution x-ray diffraction and low temperature photoluminescence measurements.

Figure. Free standing 3C-SiC and a schematic illustration of the two-stage growth process

*Valdas Jokubavicius

Department of Physics, Chemistry and Biology (IFM), Semiconductor Materials Division, Linköping University, 581 83 Linköping, Sweden

Phone: +46 13 282641

Email: valjo@ifm.liu.se

Single domain 3C-SiC growth on off-oriented 4H-SiC substrates

Valdas Jokubavicius^{,1}, Gholam R. Yazdi¹, Rickard Liljedahl¹, Ivan G. Ivanov¹, Jianwu Sun¹, Xinyu Liu¹, Philipp Schuh², Martin Wilhelm², Peter Wellmann², Rositsa Yakimova¹ and Mikael Syväjärvi¹*

¹Department of Physics, Chemistry and Biology (IFM), Semiconductor Materials Division,
Linköping University, 58 183 Linköping, Sweden

²Materials Department 6 (i-meet), Crystal Growth Lab, University of Erlangen, Martensstr. 7, D-91058 Erlangen, Germany

KEYWORDS: 3C-SiC, lateral enlargement, sublimation epitaxy, geometrical control

ABSTRACT

We investigated the formation of structural defects in thick (~ 1 mm) 3C-SiC layers grown on off-oriented 4H-SiC substrates via lateral enlargement mechanism using different growth conditions. A two-step growth process based on this technique was developed, which provides a trade-off between the growth rate and the number of defects in the 3C-SiC layers. Moreover, we

demonstrated that the two-step growth process combined with geometrically controlled lateral enlargement mechanism allows formation of single 3C-SiC domain which enlarges and completely covers the substrate surface. High crystalline quality of the grown 3C-SiC layers is confirmed using high resolution x-ray diffraction and low temperature photoluminescence measurements.

1. INTRODUCTION

The great challenge to obtain high crystalline quality cubic silicon carbide (3C-SiC) has hampered its use in semiconductor applications.¹⁻⁴ In order to accelerate the 3C-SiC application in electronics high quality thick 3C-SiC layers or substrates are needed. They could be used for homoepitaxial growth, e.g., by chemical vapor deposition (CVD) which allows reproducible growth of device quality 3C-SiC layers. In addition, thick layers could be explored as seeds in bulk growth techniques like seeded sublimation growth to obtain large 3C-SiC crystals/boules. However, thick layers of 3C-SiC with quality similar to that in commercially available hexagonal (4H- and 6H) SiC substrates have not been demonstrated.

There are fundamental challenges in the growth of single crystal 3C-SiC. Heteroepitaxial layers of 3C-SiC grown on silicon substrates contain high density of structural defects due to a large mismatch in lattice parameter ($\sim 20\%$) and thermal expansion coefficient ($\sim 8\%$). In contrast, the mismatch problems are substantially smaller when using hexagonal SiC substrates (in-plane lattice mismatch $\sim 0.08\%$ for 3C/4H).⁵ However, despite promising results,⁶⁻⁹ the control of initial nucleation of 3C-SiC domains on hexagonal SiC, especially when growing on

nominally on-axis substrates, and the reproducibility of high crystalline quality layers, in particular thick ones, remain problematic.

Recently, a generic concept of producing 3C-SiC layers with substantially less number of domains, compared to the 3C-SiC grown on nominally on-axis substrates, has been demonstrated using a lateral enlargement (LE) mechanism on off-oriented hexagonal SiC substrates.¹⁰ The LE mechanism allows to localize the initial nucleation of 3C-SiC domains on an *in situ* formed large terrace with an on-axis area at the edge of hexagonal substrate. These domains enlarges along the step-flow [11-20] direction and completely cover the surface. It was shown that a reproducible growth of 3C-SiC layers without foreign polytype inclusions can be obtained using this approach. However, even though substantially reduced in number, the layers still contain incoherent twin boundaries, also called double positioning boundaries (DPBs), which have a pronounced influence on electrical characteristics^{11, 12} and thus have to be eliminated in order to unleash the full potential of 3C-SiC for various applications.

In this paper we present a two-step process combined with a geometrically controlled LE mechanism that leads to the growth of *single domain* 3C-SiC layers. Such 3C-SiC growth approach has been developed on the ground of detailed analysis of the formation of various structural defects in 3C-SiC layers grown under different growth conditions and different growth arrangements. In addition, we demonstrate that 3C-SiC layers with profound thickness (>1 mm) can be grown and used to obtain free-standing 3C-SiC substrates.

2. EXPERIMENTAL DETAILS

The 3C-SiC layers were grown via LE mechanism using the sublimation epitaxial growth technique.¹⁰ The schematic illustration of the growth setup is shown in Figure 1. The materials

are placed inside an inductively heated graphite crucible on top of each other in a sandwich-like arrangement with a tantalum foil at the bottom, followed by a polycrystalline SiC plate (source material), a graphite spacer with an opening for vapor species transport, a substrate and a graphite plate to prevent backside sublimation of the substrate. The tantalum foil acts as a carbon getter at elevated temperatures and leads to an increased concentration of silicon in the vapor phase inside the crucible. This is beneficial for the cubic polytype stabilization and expands the growth parameters window in which the graphitization of the source and substrate surfaces can be avoided.^{13, 14} In all experiments, 4H-SiC substrates with a 4 degree surface off-orientation from (0001) toward $\langle 11\text{-}20 \rangle$ direction were used. Spacers with different types of opening shapes and thickness varying from 1 to 2 mm were explored. The growth temperatures were ranging from 1800 to 1950°C and growth times up to 10 hours were used.

Figure 1. Schematic illustration of 3C-SiC growth setup.

The surface morphology of the samples was investigated using an optical microscope with Nomarski interference contrast and scanning electron microscope (SEM). The crystalline quality was assessed by high resolution X-ray diffraction (HRXRD). The average values of the full width at half-maximum (FWHM) of ω rocking curves obtained on five different points on each samples using (111) Bragg reflection and a footprint of $1 \times 2.7 \text{ mm}^2$ were used as indicators for

the crystalline quality of 3C-SiC layers. In addition, low temperature photoluminescence (LTPL) at a temperature of 2 K with the samples immersed in pumped liquid helium, using as an excitation the 351 nm line of an Ar-ion laser. The 3C-SiC layers were also analyzed using Raman spectroscopy using Jobin Yvon LabRAM HR-800 system with 633 nm He-Ne laser.

3. RESULTS AND DISCUSSIONS

The 3C-SiC layers grown using the LE mechanism pass through several interconnected growth stages. These include formation of a large terrace with an on-axis area at the edge of the sample, preferential nucleation of 3C-SiC domains on the large terrace, and their lateral enlargement along the step-flow direction (Figure 2a). Therefore, the ultimate goal for obtaining high quality layer is the formation of a single domain 3C-SiC on the large terrace. If such DPB-free domain is developed and its lateral enlargement pathway is free of obstacles or crystallographic defects, a single domain 3C-SiC layer can be grown.

Figure 2. (a) Schematic illustration of 3C-SiC layer development, b) optical micrograph of a 3C-SiC sample with a surface area of $7 \times 7 \text{ mm}^2$.

Previously, the growth of 3C-SiC layers was demonstrated using the original LE growth arrangement that was based on a squared spacer opening.¹⁰ The layers grown using such

arrangement still contain a few DPBs which propagate along the step-flow direction and leave several elongated surface defects in the resultant layer as seen in Figure 2b. To reduce and finally eliminate such defects, in the present work, we have: i) studied the formation mechanism of DPBs and other structural defects in thick (up to 1 mm) 3C-SiC layers grown using different growth conditions, and ii) developed a two-step growth process which combined with geometrically controlled LE mechanism leads to growth of single domain 3C-SiC layers.

3.1 Structural defects analysis in thick 3C-SiC layers. In order to understand how we could further improve the structural quality of 3C-SiC layers and optimize the LE mechanism in the original growth arrangement, we have conducted a study on samples grown using different growth rates, which in sublimation epitaxy are mainly governed by the growth temperature.¹⁵

The majority of DPBs in 3C-SiC layers grown via the LE mechanism originate at the edge of the sample during the initial formation of the 3C-SiC and propagate along the step-flow direction as shown in Figure 3a. Additional 3C-SiC domains/inclusions may also occur in the central part of the layer. They are indicated as parasitic 3C-SiC (p-3C) in Figure 3a. The formation of p-3C can be induced by various crystallographic defects, mechanical damage or solid particles present on the surface of the 4H-SiC substrate. They act as obstacles for propagating steps. Therefore, the step-flow is suppressed at the obstacle and a small on-axis area, that is a preferential 3C-SiC nucleation site, is created. If DPB propagating from the edge of the sample interact with p-3C, the result is a cascade of multiple structural defects that propagate along the step-flow direction and deteriorate the epitaxial layer.

In general, the DPBs observed on about 1 mm thick 3C-SiC layer surfaces can be categorized into “open” (V-shape) and “closed” (line-like) types as indicated in Figure 3b. On the surface the

“open” type DPBs tend to broaden with an increase in layer thickness, while the “closed” type remains as line-like defect having a width which is almost independent of the layer thickness. This can be seen in cross sectional images taken from the stripes cut perpendicular to the step-flow direction at three different areas indicated as “A-A”, “B-B” and “C-C” in Figure 3b. The “A-A” cut was done at the very edge of the layer where the large terrace with an on-axis area develops and the initial formation of 3C-SiC domains takes place. A rough interface between the 3C-SiC and 4H-SiC in the “A-A” cross sectional view indicates that there is a strong competition between these two polytypes during the initial growth stage.

Figure 3. Optical micrographs: (a) surface of 3C-SiC layer with DPBs and parasitic 3C-SiC (p-3C) inclusions, (b) cross sectional views of 3C-SiC layer, (c) enlarged view of “open” and (d)

”closed” type DPBs. (e) Atomistic illustration of “open” and “closed” type DPBs formation during the initial growth stage.

In the cross sectional view of area ”B-B” as shown in Figure 3b, the “open” (V-shape) and “closed ” (line-like) type DPBs and the transition layer (indicated as “TL”) between the 3C- and 4H-SiC are clearly visible. The change in the TL thickness is abrupt at points where DPBs are formed. There is a variation in TL thickness over the entire length of the 3C-SiC layer. This is seen in the cross sectional view of “C-C” in Figure 3b where the transition layer is thicker, but its profile observed in the cross sectional view of “B-B” is maintained.

The type of DPB (“open” or “closed”) could be determined during the initial stage of 3C-SiC formation on the large terrace. This is clearly indicated in Figures 3c-d which show higher magnification cross sectional views of stripes that are cut perpendicular to the step-flow direction at the edge of the 3C-SiC layer where the large terrace is formed. The DPBs are surrounded by line-fringes (dashed lines in Figure 3c-d as guide for the eye) which form either as open- or closed-V-shape defects. Such fringes are usually attributed to agglomeration of stacking faults or microtwins around incoherent twin boundaries.¹⁶ During the initial formation of 3C-SiC on the large terrace, the 3C-SiC domains can nucleate in two equally possible orientations rotated by 60° on (0001) plane due to two possible stacking orders of ABCABC and ACBACB along the [0001] direction. In Figure 3e such 60°-rotated domains are indicated as (I) and (II). Despite the rotation of domains, they have an enhanced lateral enlargement along the step-flow direction. At the same time they enlarge perpendicularly to the step-flow growth direction. Depending on the 3C-SiC domains rotation and the side from which they approach each other in perpendicular to the step-flow direction the neighboring domains are inclined towards (“closed”) or outwards

(“open”) with respect to each other along the c-axis as shown in Figure 3e. Therefore, if the DPBs are scanned perpendicular to the step-flow direction from one edge of the sample to the other edge, it can be observed that every second DPB originating from the very edge of the terrace possesses the same V-shape.

In order to understand further details of their formation, a series of 3C-SiC samples with 1 mm thickness were grown using different growth temperatures in the range from 1800°C to 1950°C. As seen in Figure 4a the growth rate almost doubles if the growth temperature is increased by 50°C. Therefore, the growth time needed to obtain 1 mm thick layer at 1800°C is about 10 hours while it is only about 1 hour at 1950°C. The number of DPBs (counted using an optical microscope on the large terrace area) increases by increasing the growth temperature/growth rate (Figure 4b). The supersaturation increases with the increase in the growth temperature/growth rate and this leads to a higher density of 3C-SiC nuclei and consequently higher density of DPBs which are formed on the large terrace. This indicates that lower growth temperatures/growth rates should be used for growth of high quality layers with minimized number of DPBs. However, there is a threshold in the growth rate below which the stability of the cubic polytype cannot be maintained. This was observed when 3C-SiC layers were grown at a growth rate lower than 100 $\mu\text{m/h}$. In this case, the 3C-SiC that is formed at the edge of the sample contains foreign polytype inclusions which propagate along the step-flow direction. In addition, there is also an upper limit in the growth rate at which various structural defects start to appear to a substantially higher degree. For example, the 3C-SiC layers grown at the temperature of 1950°C (corresponding to a growth rate of $\sim 1 \text{ mm/h}$) exhibit significantly higher density of parasitic 3C-SiC inclusions in the center of the sample.

Figure 4. (a) Growth rate vs temperature, (b) number of DPBs per large terrace area vs growth temperature.

Another type of macro-defects which can be observed on the surface of the 3C-SiC layers are line-like defects. These are visible only at the very edge of the sample on the right side in Figure 3a and b. Such defects form via several development stages in which the transition layer plays an important role. A completely developed 3C-SiC layer may be viewed as a three-layer system, where there is a homoepitaxial 4H-SiC layer at the bottom, which is followed by the transition layer and the 3C-SiC layer on the top. The transition layer enlarges laterally approximately two times faster than the 3C-SiC layer.¹⁰ The growth front of the transition layer contains a rough surface with an elongated groove-like pattern. This is shown in the SEM micrograph in Figure 5a which was obtained from the surface of a sample with low 3C-SiC coverage and a total layer thickness of 250 μm . The groove-like pattern becomes more pronounced when the transition layer propagates along the step-flow growth direction and approaches the opposite edge that is shown in Figure 5b. Moreover, the groove-like pattern is accompanied by extended defects (ED in Figure 5b). The origin of these defects is threading defects (indicated as “MD” in the cross

section view of “C-C” in Figure 3b) which are propagating in the 4H-SiC homoepitaxial layer. Due to the pronounced groove-like pattern at the edge, the part of 3C-SiC which contains the most defects is also located at this edge. The density of these extended defects varies from sample to sample and does not correlate clearly with the growth parameters. Therefore, other factors like microscopic defects in the substrate or built-up stress between the homoepitaxial and transition layers could be causing the formation of such defects.

Figure 5. SEM micrographs of (a) transition layer growth front (total layer thickness $\sim 250\ \mu\text{m}$), (b) extended defects (ED) (total layer thickness $\sim 1\ \text{mm}$). (c) Raman spectra measured on different positions along the step-flow direction in 3C-SiC layer (thickness $\sim 900\ \mu\text{m}$), (d) enlarged view of the Raman spectra obtained on points 1, 8 and 14.

Micro-Raman spectroscopy in the back scattering geometry was used to scan a 3C-SiC layer (thickness $\sim 900\text{ }\mu\text{m}$) that contains extended defects as shown in Figure 5b. As seen in Figure 5c, the Raman spectra change significantly when scanning the layer along the step-flow direction (from point 1 to point 14). In Figure 5d a more detailed view of the Raman peaks obtained from three measurement points (1, 8, and 14) is presented. The inset above the Raman spectrum of point 1 shows a small peak at 776 cm^{-1} which corresponds to the folded transverse optical (FTO) mode of 4H-SiC¹⁷ and is therefore attributed to contribution from the substrate. Its appearance is expected in view of the fact that both 3C- and 4H-SiC are transparent for the exciting 633 nm laser beam,¹⁸ and its gradual intensity increase from point 1 to point 14 is in line with the decreasing 3C-SiC layer thickness. The line observed at 767 cm^{-1} for points 8 and 14 corresponds to the FTO of 6H-SiC. This line also gets stronger when moving the laser beam from point 1 to 14 along the step-flow direction and is most likely due to the transition layer which is buried under the 3C-SiC layer but approaches the sample surface in the thinnest part (point 14).

The FLO mode of 3C-SiC at 972 cm^{-1} remains at the same position for all spectra measured at points 1-12. This indicates that at these points the surface of the layer is fully covered with 3C-SiC. A significant change in the Raman spectra is observed at the opposite edge of the sample where the 3C-SiC layer is thin. This location contains extended defects and the transition layer is the thickest. A strong FTO mode of 6H-SiC at 767 cm^{-1} is seen in the spectra measured at points 13 and 14. The FLO peak of 3C-SiC, which remains un-shifted at 972 cm^{-1} for points 1–12, downshifts to $967 - 968\text{ cm}^{-1}$ for points 13 and 14. This indicates that the Raman spectrum becomes dominated by other polytypes from the transition layer. Also, a broader line peaking

around 789 cm^{-1} can be observed at points 13 and 14, which most probably originates from an overlap of the FTO modes of a mixture of polytypes present in the transition layer (e.g., 21R-, 6H- and 15R-SiC at 791 , 789 and 785 cm^{-1} , respectively).¹⁷

While DPBs are the most prominent, the next most important defects in 3C-SiC are stacking faults (SFs). The 3C-SiC has the lowest SFs formation energy, which varies from -1.71 to -6.27 mJ/m^2 compared to 3.1 to 40.1 mJ/m^2 in 6H-SiC and 17.7 to 18.7 mJ/m^2 in 4H-SiC.¹⁹ It has been demonstrated that the density of SFs can be reduced in 3C-SiC grown on patterned Si substrates.^{20, 21} Small SF-free 3C-SiC areas can be grown on a step-free 4H-SiC mesas.²² However, to our knowledge there is no data on large-area SF-free 3C-SiC layers.

Molten potassium hydroxide (KOH) was used to reveal stacking faults in 3C-SiC layers grown at three different temperatures/growth rates. Stripes along the step-flow direction were cut from a single domain area and etched in molten KOH at 500°C for 1 min. In such a way SFs on two perpendicular surfaces, which corresponds to hexagonal (0001) and (1-100) planes, were revealed in a single sample. On the (0001) surface, which corresponds to (111) in the 3C-SiC layer, the SFs occur as lines which are forming one or more sides of equilateral triangles whose density depends mainly on the thickness of the 3C-SiC layer rather than on growth parameters (Figure 6a-c). The highest density of triangular features is observed on the right side (which corresponds to the thinnest part of the 3C-SiC layer) of each stripe and gradually decreases with an increase in the layer thickness. This reflects that the highest number of stacking faults is formed at the transition layer/3C-SiC interface. It is likely that there is a mismatch caused by the 3C-SiC and the transition layer. The relief of mismatch strain results in formation of stacking faults. The same thickness dependent density trend of triangular features was observed on etched (1-100) surfaces. A representative picture of such etched 3C-SiC surface is shown in Figure 6d.

The decrease of stacking fault density with the increase in layer thickness suggests that the growth of bulk 3C-SiC could be a way to further reduce stacking faults.

Figure 6. Optical micrograph of KOH etched 3C-SiC (111) surfaces, which correspond to hexagonal (0001), grown at (a) 1800°C, (b) 1850°C and (c) 1900°C, (d) optical micrograph of KOH etched 3C-SiC surface grown at 1850°C which corresponds to hexagonal (1-100).

3.2 Two-step process. As demonstrated in the analysis of defects in the previous section, the formation of DPBs can be controlled by changing growth parameters, while the density of triangular features, which are imprints of SFs in 3C-SiC (111), depends mainly on the layer thickness. The formation of other crystallographic defects can be correlated with the quality of the substrate surface. Based on the study shown in Figure 4, the 3C-SiC layers should be grown at 1800°C which in our sublimation growth setup has a growth rate of about 100 μm/h and resulted in a low number of DPBs formed on the large terrace. However, at such growth rate the growth time needed to obtain a layer with a thickness of 1 mm is 10 hours. In order to demonstrate thick 3C-SiC growth at an industrially attractive growth rate, a two-step growth process was introduced. A detailed breakdown of the growth process is presented in Figure 7.

Figure 7. Two-step growth process of 3C-SiC layers with a temperature ramp up and ramp down steps.

The area indicated as “I” (Figure 7) corresponds to the temperature ramp up at a rate of 20 °C/min up to the growth temperature of 1800°C. This growth temperature was maintained for 1 hour and during this time (area marked as “II” in Figure 7), a 3C-SiC growth front with a low DPB density is formed. After that, the temperature is increased to 1900°C and maintained for 1 hour and 45 min (“III” in Figure 7). During this step, the growth rate increases from ~100 $\mu\text{m/h}$ to ~500 $\mu\text{m/h}$, which corresponds to 3C-SiC lateral enlargement rate of ~3.5 mm/h. After the growth is completed, the induction heating is switched off and the layer is cooled down (Figure 7 “IV”). The quality, in terms of DPBs, of 3C-SiC layers grown using such two-step process, is very similar to the layers grown at 1800°C, while the time (excluding temperature ramp-up and cooling down) is reduced from 10 hours to 2 hours 45 min.

3.3 Geometrically controlled lateral enlargement. It has been demonstrated that the control of 3C-SiC nucleation using CVD growth over a small area can be obtained by patterning the surface of a 4H-SiC substrate using photolithography to form mesas in different geometries.^{23, 24} Initial results of the effect of the graphite spacer opening shape in 3C-SiC nucleation using

sublimation epitaxy on low off-axis 6H-SiC substrates have been also shown.²⁵ Here we explore a geometrical control and demonstrate that different spacer shaping can be applied to promote formation of only one 3C-SiC domain that enlarges and completely covers the surface of the epilayer.

In the original 3C-SiC lateral enlargement growth setup, the substrate is placed on the spacer in such a way that the step-flow direction is perpendicular to the edge of the spacer opening as shown in Figure 8a. In this case, the initial 3C-SiC domains form on the large terrace with an on-axis surface along the edge of the layer. Ideally, only one nucleation center/domain of 3C-SiC on the terrace would form. However, several 3C-SiC domains always form due to the large surface area of the terrace. In order to avoid this, two conditions are required: i) the growth parameters should be adjusted to form a minimum number of 3C-SiC domains on the terrace during the initial growth, and ii) the area on which 3C-SiC domains form should be minimal to facilitate single-domain formation. The first condition can be met by using two-step process which allows to reduce the number of 3C-SiC domains while the second condition prompts for changes in the geometrical arrangement in the growth cell, namely, in the shape of the opening in the spacer.

In our growth concept a terrace with an on-axis surface preferentially forms along the edge of the spacer opening which is perpendicular to the step-flow direction as shown in Figure 8a. In order to reduce the surface area of the terrace, two other shapes of the spacer opening were explored. The first one is the same squared opening as the original one, but rotated by 45 degrees (Figure 8b) with respect to the [11-20] direction. The idea for using such spacer is to form a small on-axis area at the corner of the substrate at which the nucleation begins. The second opening has a circular shape (Figure 8c). In this case, the size of the terrace is larger than the one given by the 45 degree rotation opening, but smaller than in the original one.

The comparative results are shown in Figure 8d-f. The growth times were adjusted to have a layer thickness of 1.2 mm using the original (Figure 8a) and circular (Figure 8c) spacer openings, and 1.4 mm using the 45 deg rotated spacer (Figure 8b). In the latter case a larger thickness is needed to ensure a complete surface coverage with 3C-SiC due to the longer distance the 3C-SiC domain needs to travel along the diagonal of the square. The 3C-SiC samples shown in Figure 8d-f are free-standing layers obtained by polishing away the 4H-SiC substrate.

Figure 8. (a-c) Schematic illustration of spacer and substrate arrangements. Optical micrographs of the freestanding 3C-SiC grown using (d) original (e), 45 degree rotated and (f) circular spacer openings. Black arrows indicate step-flow growth direction.

Clearly, the number of domains is substantially decreased in both non-original arrangements. In fact, we have obtained a single domain growth. However, parasitic 3C-SiC inclusions, seen as lines in the center of samples in Figure 8e-f, may still form on the surface. Similarly to homoepitaxial growth in high growth rate epitaxy on 6H and 4H-SiC¹⁵, we believe they are

originating from the defects in the substrate or are caused by residual contaminants on the substrate surface after the chemical cleaning process.

Figure 9. LTPL spectrum of 3C-SiC. The inset shows $I_{LA/TO}$ ratios measured on three different areas on each sample shown in Figure 7d-f. The “Large terrace” area represents the thickest and the “Edge” the thinnest part of the 3C-SiC layer on the sample.

In order to investigate if the shape of the layer induces any changes in the 3C-SiC material quality we carried out LTPL measurements at 2K. Three spectra from three locations were obtained for each sample: i) at the edge where the large terrace is formed and 3C-SiC has largest thickness, ii) in the center of the sample and iii) at the opposite edge with the thinnest part of 3C-SiC layer. Due to the low penetration depth of the exciting laser (351 nm) no contribution from other SiC polytypes but 3C-SiC could be detected in the spectra. Each spectrum demonstrates well resolved near-band-edge features and lines associated with multiple bound-exciton complexes with up to four electron-hole pairs indicating high quality of 3C-SiC material.^{26, 27} A spectrum representative for all samples is displayed in Figure 9. Nitrogen concentration of 6-

$8 \times 10^{15} \text{ cm}^{-3}$ was estimated in all samples using the FWHM of the TA-phonon replica.²⁸ Moreover, we have observed that the biaxial stress, which can be estimated using the $I_{\text{LA}}/I_{\text{TO}}$ intensity ratio,²⁹ varies along the step-flow direction in each sample as presented in the inset table in Figure 9. The $I_{\text{LA}}/I_{\text{TO}}$ ratio shows a clear dependence of biaxial stress on the thickness of the 3C-SiC and approaches a value of one (which reflects that biaxial stress more or less vanishes) when the thickness of the 3C-SiC layer is about 1.2 mm. Based on $I_{\text{LA}}/I_{\text{TO}}$ values presented in the inset table, we cannot distinguish if any of the shapes induces higher or lower overall biaxial stress than the others. For instance, the original and circular 3C-SiC layers have similar total thicknesses. However, there can be some thickness variations leading to different $I_{\text{LA}}/I_{\text{TO}}$ values, when measuring, for example, at the “center” location in both 3C-SiC layers. Nevertheless, we can conclude that all three samples possess very similar crystalline quality which is also confirmed by HRXRD in the next section.

3.4 Comparison of different 3C-SiC growth schemes. The experimental work presented in previous sections allowed us to explore the formation of various structural defects and propose growth schemes for the improvement of the original LE mechanism. In Table 1, we present a summary of different growth schemes. As demonstrated in our previous study, the 3C-SiC layers grown using the original LE mechanism show state of the art quality compared to 3C-SiC grown on silicon or hexagonal silicon carbide substrates.¹⁰ However, the original LE mechanism (growth rate $\sim 0.5 \text{ mm/h}$) cannot realize growth of single domain 3C-SiC layers due to a multiple 3C-SiC domains formation on the large terrace. A single 3C-SiC domain on the terrace area was achieved only by combining the two-step process with a geometrically controlled LE mechanism at an average growth rate of $\sim 0.36 \text{ mm/h}$. While we managed to control DPBs on the terrace

area, elimination of other structural defects needs additional studies. We have observed that the density of triangular defects (imprints of the SFs) revealed by KOH etching is rather thickness- than processdependent in all growth schemes. Parasitic 3C-SiC (p-3C) inclusion nucleation in the center of the sample is mainly determined by the substrate surface quality. This is also an issue in formation of defects (ED and MD) at the edge opposite to the large terrace. Nevertheless, the combination of the two-step process and a geometrically controlled lateral enlargement mechanism allows production of single domain 3C-SiC layers which can be explored in homoepitaxy for devices or as seeds for the bulk growth of 3C-SiC crystals.

Table 1. Summary of different 3C-SiC growth schemes and material characteristics.

	original LE mechanism	two-step process + geometrical control	
spacer opening	original (squared - $7 \times 7 \text{ mm}^2$)	45 deg rotated (squared - $7 \times 7 \text{ mm}^2$)	circular (diameter - 7 mm)
avg. growth rate ($\mu\text{m/h}$)	~500	~360	~360
DPBs/terrace area	up to 4	0	0
SFs revealed by KOH etching	3C-SiC layer thickness dependent		
p-3Cs per sample	substrate surface quality related		
MDs and EDs at the edge of sample	substrate quality and 3C-SiC sample structure related		
HRXRD (avg. fwhm (arcsec))	40	38	38
LTPL	100% surface coverage with 3C-SiC and multiple bound-exciton complexes with up to four electron-hole pairs in all layers		

4. CONCLUSIONS

Growth of single domain 3C-SiC layers was achieved by a combination of different growth schemes. These schemes were developed by studying structural defects in thick (~up to 1 mm) 3C-SiC layers grown using different growth conditions via an original lateral enlargement mechanism. We have observed that the density of DPBs can be reduced by lowering the growth rate, while SFs density mainly depends on the layer thickness. Furthermore, we have explained the formation of extended defects which are observed at the very edge on the surface of 3C-SiC layers. On the basis of the results of structural defects formation in thick 3C-SiC grown using different growth conditions, we have developed a two-step process that allows reduction of DPBs on the large terrace. A complete elimination of DPBs on the large terrace or formation of only one 3C-SiC domain that enlarges and covers the complete surface was achieved by combining the two-step process with the geometrically controlled lateral enlargement mechanism. In this way, single domain 3C-SiC layers with a squared ($7 \times 7 \text{ mm}^2$) or circular shape (diameter 7 mm) and a total layer thickness up to 1.4 mm were obtained. As demonstrated by HRXRD (average value of fwhm of ω rocking curves is 38 arcsec) and LTPL measurement data, the layers possess high crystalline quality.

AUTHOR INFORMATION

Corresponding Author

*valjo@ifm.liu.se

Funding Sources

The Swedish Energy Agency, Swedish Research Council and the Swedish Governmental Agency for Innovation Systems (Vinnova).

REFERENCES

[1]Kato, M.; Yasuda, T.; Miyake, K.; Ichimura, M.; Hatayama, T. *Int J Hydrogen Energy* **2014**,39, 4845-4849.

[2]Saddow, S. E.; Frewin, C. L.; Coletti, C.; Schettini, N.; Weeber, E.; Oliveros, A.; Jarosezski, M. *Mater. Sci. Forum* **2011**,679 - 680, 824.

[3]Beaucarne, G.; Brown, A. S.; Keevers, M. J.; Corkish, R.; Green, M. A. *Prog Photovoltaics Res Appl* **2002**,10, 345-353.

[4]Schöner, A.; Krieger, M.; Pensl, G.; Abe, M.; Nagasawa, H. *Chem. Vapor Depos.* **2006**,12, 523-530.

[5]Powell, J. A.; Neudeck, P. G.; Trunek, A. J.; Beheim, G. M.; Matus, L. G.; Hoffman, R. W.; Keys, L. J. *Appl. Phys. Lett.* **2000**,77, 1449-1451.

[6]Soueidan, M.; Ferro, G. *Adv. Funct. Mater.* **2006**,16, 975-979.

- [7]Chaussende, D.; Latu-Romain, L.; Auvray, L.; Ucar, M.; Pons, M.; Madar, M. *Mater. Sci. Forum* **2005**,483, 225.
- [8]Leone, S.; Beyer, F. C.; Henry, A.; Kordina, O.; Janzén, E. *Phys. Status Solidi (RRL)* **2010**,4, 305-307.
- [9]Lebedev, A. A.; Abramov, P. L.; Zubrilov, A.; Bogdanova, E. V.; Lebedev, S. P.; Seredova, N. V.; Tregubova, A. S. *Mater. Sci. Forum* **2011**,679, 12-15.
- [10]Jokubavicius, V.; Yazdi, G. R.; Liljedahl, R.; Ivanov, I. G.; Yakimova, R.; Syväjärvi, M. *Cryst. Growth Des.* **2014**,14, 6514-6520.
- [11]Kohyama, M.; Yamamoto, R. *Solid State Phenomena* **1994**,37, 55.
- [12]Vasiliauskas, R.; Mekys, A.; Malinovskis, P.; Syväjärvi, M.; Storasta, J.; Yakimova, R. *Mater. Lett.* **2012**,74, 203-205.
- [13]Vodakov, Y. A.; Roenkov, A. D.; Ramm, M. G.; Mokhov, E. N.; Makarov, Y. N. *Phys. Status Solidi B* **1997**,202, 177-200.
- [14]Karpov, S. Y.; Makarov, Y. N.; Ramm, M. S. *Phys. Status Solidi B* **1997**,202, 201-220.
- [15]Syväjärvi, M.; Yakimova, R.; Tuominen, M.; Kakanakova-Georgieva, A.; MacMillan, M. F.; Henry, A.; Wahab, Q.; Janzén, E. *J. Cryst. Growth* **1999**,197, 155-162.
- [16]Ferro, G.; Kim-Hak, O.; Lorenzzi, J.; Jegenyess, N.; Marinova, M.; Soueidan, M.; Carole, D.; Polychroniadis, E. K. *Mater. Sci. Forum* **2011**,679, 71-74.

- [17]Nakashima, S.; Harima, H. *Phys. Status Solidi A* **1997**,162, 39-64.
- [18]Harima, H. *Microelectron. Eng.* **2006**,83, 126-129.
- [19]Lindefelt, U.; Iwata, H.; Oberg, S.; Briddon, P. R. *Phys.Rev.B* **2003**,67, 155204.
- [20]D'Arrigo, G.; Severino, A.; Milazzo, G.; Bongiorno, C.; Piluso, N.; Abbondanza, G.; Mauceri, M.; Condorelli, G.; La Via, F. *Mater. Sci. Forum* **2010**,645, 135-138.
- [21]Nagasawa, H.; Yagi, K.; Kawahara, T. *J. Cryst. Growth* **2002**,237, 1244-1249.
- [22]Speer, K.; Neudeck, P.; Spry, D.; Trunek, A.; Pirouz, P. *J. Electron. Mater.* **2008**,37, 672-680.
- [23]Lorenzzy, J.; Lazar, M.; Tournier, D.; Jegenyess, N.; Carole, D.; Cauwet, F.; Ferro, G. *Cryst. Growth Des.* **2011**,11, 2177-2182.
- [24]Neudeck, P. G.; Trunek, A. J.; Spry, D. J.; Powell, J. A.; Du, H.; Skowronski, M.; Huang, X. R.; Dudley, M. *Chem. Vapor Depos.* **2006**,12, 531-540.
- [25]Jokubavicius, V.; Liljedahl, R.; Ou, Y. Y.; Ou, H. Y.; Kamiyama, S.; Yakimova, R.; Syväjärvi, M. *Mater. Sci. Forum* **2011**,679, 103-106.
- [26]Bergman, J. P.; Janzén, E.; Choyke, W. J. *Phys. Status Solidi B* **1998**,210, 407-413.
- [27]Latu-Romain, L.; Chaussende, D.; Balloud, C.; Juillaguet, S.; Rapenne, L.; Pernot, E.; Camassel, J.; Pons, M.; Madar, M. *Mater. Sci. Forum* **2006**,527, 99.

[28]Camassel, J.; Juillaguet, S.; Zielinski, M.; Balloud, C. *Chem. Vapor Depos.* **2006**,12, 549-556.

[29]Choyke, W. J.; Feng, Z. C.; Powell, J. A. *J. Appl. Phys.* **1988**,64, 3163-3175.

For Table of Contents Use Only

Single domain 3C-SiC growth on off-oriented 4H-SiC substrates

Valdas Jokubavicius*,¹, G. Reza Yazdi¹, Rickard Liljedahl¹, Ivan G. Ivanov¹, Jianwu Sun¹, Xinyu Liu¹, Philipp Schuh², Martin Wilhelm², Peter Wellmann², Rositsa Yakimova¹, Mikael Syväjärvi¹

¹Department of Physics, Chemistry and Biology (IFM), Semiconductor Materials Division, Linköping University, 581 83 Linköping, Sweden

²Materials Department 6 (i-meet), Crystal Growth Lab, University of Erlangen, Martens Straße 7, D-91058 Erlangen, Germany

A combination of a two-step process and geometrically controlled lateral enlargement mechanism allows to form a single 3C-SiC domain which enlarges and completely covers the surface of the substrate. High quality 3C-SiC layers with the thickness up to 1.4 mm have been demonstrated.