

CVD growth of 3C-SiC on 4H-SiC substrate

Anne Henry, Xun Li, Stefano Leone, Olof Kordina and Erik Janzén

Linköping University Post Print

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

Original Publication:

Anne Henry, Xun Li, Stefano Leone, Olof Kordina and Erik Janzén, CVD growth of 3C-SiC on 4H-SiC substrate, 2012, Material Science Forum, 711, 16-21 .

<http://dx.doi.org/10.4028/www.scientific.net/MSF.711.16>

Copyright: Trans Tech Publishing

Postprint available at: Linköping University Electronic Press

<http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-79057>

CVD growth of 3C-SiC on 4H-SiC substrate

Anne Henry^{1,a}, Xun Li^{1,b}, Stefano Leone^{1,c}, Olof Kordina^{1,d} and Erik Janzén^{1,e}

Department of Physics, Chemistry and Biology, Linköping University, SE-581 83 Linköping, Sweden

^aanhen@ifm.liu.se, ^bxunli@ifm.liu.se, ^cleone@ifm.liu.se, ^dolkor@ifm.liu.se, ^eerija@ifm.liu.se

Keywords: CVD, 3C/4H, layer morphology, double-position-boundaries

Abstract. The hetero epitaxial growth of 3C-SiC on nominally on-axis 4H-SiC is reported. A horizontal hot-wall CVD reactor working at low pressure is used to perform the growth experiments in a temperature range of 1200-1500 °C with the standard chemistry using silane and propane as precursors carried by a mix of hydrogen and argon. The optimal temperature for single-domain growth is found to be about 1350 °C. The ramp up-conditions and the gas-ambient atmosphere when the temperature increases are key factors for the quality of the obtained 3C layers. The best pre-growth ambient found is carbon rich environment; however time of this pre-treatment is crucial. A too high C/Si ratio during growth led to polycrystalline material whereas for too low C/Si ratios Si cluster formation is observed on the surface. The addition of nitrogen gas is also explored.

Introduction

3C-SiC has been one of the most studied polytypes of SiC since it can be easily grown on inexpensive silicon substrates. However, when grown on Si substrates, due to the large differences in lattice constant (20%) and thermal expansion coefficient (8%) the quality of the layer is very poor. This is generally observed as formation of several crystallographic defects such as anti-phase domains, stacking faults and micro-twins. The 3C polytype could still be of interest for its high electron drift velocity (calculated to be above 2×10^7 cm/s) [1] and electron mobility (about 1000 cm²/Vs) [2], a fact which will have some advantages for MOSFET devices. Higher quality 3C layers can be grown on the most common SiC hexagonal-polytype substrates, which has been demonstrated by vapor-liquid-solid (VLS) [3], sublimation epitaxy [4] and chemical-vapor-deposition (CVD) [5-8]. However, double-position-boundaries (DPB) which is a twinning of the grown layer, is still a problem in thin 3C epilayers grown on hexagonal substrates. Those studies have used mainly nominally on-axis 6H-SiC as substrates. However, earlier and at a rather high growth temperature of about 1500-1550 °C, Nishino et al [5] reported that using 15R substrates fewer DPBs were noticed on the layer surface, compared to 6H substrates. Besides, the DPBs density was decreasing with increasing 3C layer thickness, with the formation of defects having a hexagonal shape for thin layers and transforming into a triangular shape. In addition two-dimensional electron gas (2DEG) was predicted [9] to be formed at the hetero-junction 4H/3C or 6H/3C SiC due to abrupt changes in spontaneous polarization between the cubic and the hexagonal SiC. This has been demonstrated for 3C grown on C face 6H SiC [7] whereas a two-dimensional hole gas (2DHG) appeared when using Si face 4H SiC as substrate [6]. Those studies were done for undoped 3C layers which have always n-type conductivity. However, when growing p-doped 3C epilayer on Si-face n-type 6H substrate, 2DEG formation was proposed to be formed at the hetero-junction [10]. In this study the epitaxial growth of 3C-SiC on nominally on-axis 4H-SiC is reported using standard chemistry.

Experimental conditions

In this study the epitaxial growths are done in a horizontal hot-wall reactor with a RF-heated tapered susceptor. We have used standard chemistry with silane (SiH₄) and propane (C₃H₈) as

precursors carried by a mixture of hydrogen and argon (about 2% of Ar). The growth is done at reduced pressure, typically 200 mbar. The used substrates are Si-face nominally on-axis 4H-SiC materials. This Si-face is for the hexagonal polytype generally chosen to get lower net doping concentration; investigation of the growth 3C on C-face material is not reported here. Several growth parameters are explored. The growth temperature is varied in the range 1200-1500 °C. When the temperature increased from room temperature to the growth temperature different ambient conditions were investigated, such as pure H₂ ambient or with addition of C precursor with different amounts introduced at different temperatures. The addition of a small amount of nitrogen gas was generally used. The morphology and quality of the material were analyzed by Nomarski microscopy and low temperature photoluminescence (LTPL) excited by the 244 nm or the 351 nm line of an Ar⁺ ion laser at 2K. Surface roughness was measured by atomic force microscopy (AFM). The thickness of the epilayers was evaluated by FTIR reflectance or measured from cross section. All results presented here are from layers which have a maximum thickness of 20 μm. Doping concentration was measured by Hg probe Capacitance-Voltage (CV) method at room temperature.

Experimental results

Temperature effect. The growth temperature was varied in the range 1200 °C to 1500 °C which influenced the morphology of the grown epilayers. Fig.1 shows typical Nomarski images recorded on those epilayers' surfaces. At low temperature as 1325 °C or below, the surface of the epilayer was dark brown in color (Fig.1.a). This is assumed to be due to C-rich conditions at the surface even if the C/Si at the inlet was close to 1. In the high growth temperature range close to 1400 °C the formation of a polycrystalline layer was very likely to occur, as displayed in Fig.1.d. The intermediate temperature range close to 1350 °C was the best suited for growing films with uniform morphology. However, depending on the other growth conditions (ambient during temperature ramp-up, C/Si ratio and/or addition of nitrogen) the epi-surface could be characterized by the presence of DPBs (see for instance Fig.2.a) or with large single domain as in Fig.1.c containing stacking faults (SF). On epilayers grown at 1375 °C defects were observed at the epi-surface (Fig.1.c) which are suggested to be the origin of the polycrystalline features observed when growing at higher temperatures.

C/Si ratio effect. The use of a low C/Si of 0.9 at the inlet resulted in the formation of Si clusters or droplets on the epi-surface, whereas the surface morphology of the layer grown with high C/Si of 1.1 was typically with large DPBs.

Temperature ramp up. The ambient during the temperature ramp up was shown to be critical when growing 3C-SiC on Si substrate and the carbonization layer has been introduced and is

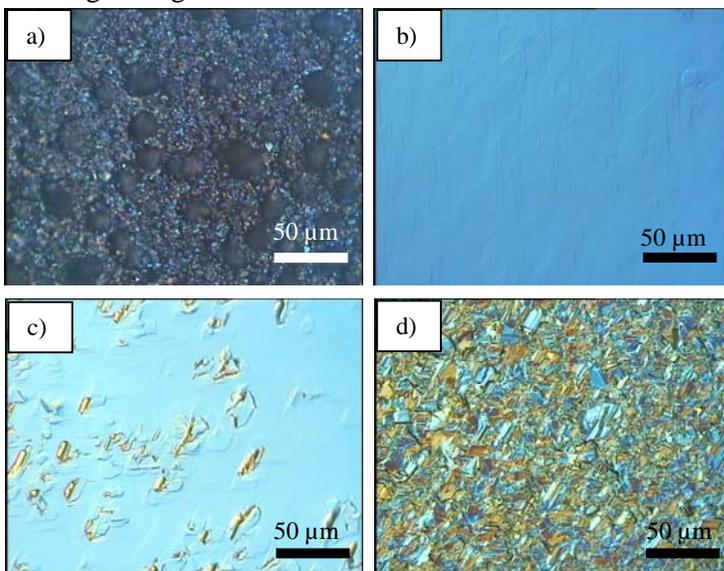


Fig.1: Nomarski images of 3C-SiC epilayers grown on 4H (0001) SiC substrates with C/Si = 1.01, Si/H₂ = 0.02%, C/N = 0.32 %, and the same temperature ramp-up conditions (C rich) and at a growth temperature of a) 1325, b) 1350, c) 1375 and d) 1400 °C, respectively. The thickness of the epilayers is about 20 μm, except for c) which is 12 μm thick (the growth time was reduced compared to the other growth runs).

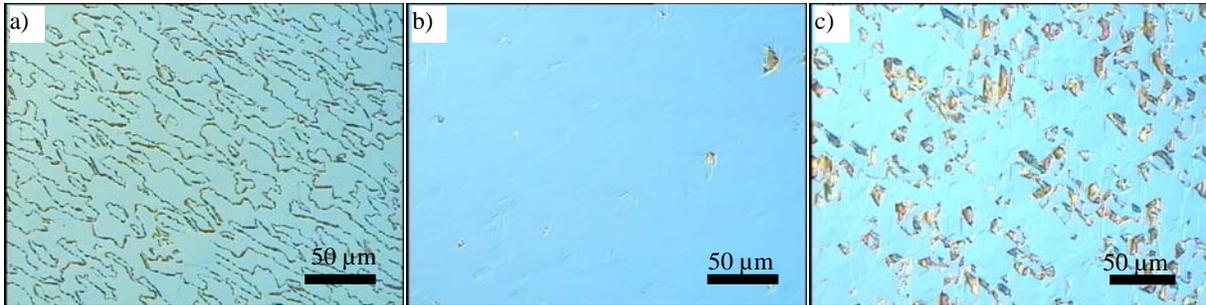


Fig.2: Nomarski images of 3C-SiC epilayers grown on 4H (0001) SiC substrates with the same growth conditions (1350 °C, C/Si = 1, Si/H₂ = 0.015%) but with different C₃H₈ flows during the temperature ramp-up as a) 3 sccm, b) 7 sccm and c) 20 sccm, respectively (note that the layers were a) 4 μm, b) and c) 15 μm. The black bars represent 50 μm

necessary for the growth of monocrystalline material [11]. However even when using (111) Si as substrate the flow of the C precursor at the early stage of the carbonization step can influence the formation and the size of the DPBs domains [12] whereas the appearance of SFs and twins were found to be independent on the carbonization conditions. Experiments done with the chloride-based process on 6H-SiC substrates also showed the importance of a carbon rich ambient during the temperature ramp up [13]. The C- precursor was first introduced at room temperature and various flows were tested. Fig.2 shows the images of the surface layers for this experiment (note that those surfaces are from 3C-SiC epilayers and not from the substrate just after the temperature ramp-up). For high flow of C₃H₈, higher than those used during the epitaxial growth itself, the morphology suffered from many DPBs and also surface defects (Fig.2.c) which could turn the appearance and quality of the epi-surface to be a polycrystalline layer, or with a brown color as in the case of the low temperature growth. This high flow of C-precursor was also introduced at different temperatures during the temperature ramp-up and most often giving rise to disordered domains. For very low flows of C₃H₈ (Fig.2.a) or when the ambient only contained carrier gases (Fig.3.a) several disordered domains were observed on the top surface of the grown layers. When C₃H₈ was added to the carrier gases, with the same flow which was used during the growth, a smooth surface with few defects was obtained (see Fig.2.b). The introduction of the C-precursor with the same flow as used during growth was also tested for different times at the growth temperature prior to the growth, meaning prior to the introduction of the SiH₄ gas. Results are displayed in Fig.3. As mentioned before, if the temperature ramp-up was done with only carrier gases (H₂+Ar) and if the growth started immediately when the temperature reached the growth temperature, DPBs domains were observed and, as in the case of Fig.3.a, sometimes they could be oriented in a particular direction. C-rich ambient condition of more than 10 minutes prior the growth was detrimental to the epitaxial growth, since disordered DPBs were easily formed (Fig.3.c). A shorter time close to 5 minutes helped to produce epilayer with smooth surface as shown in Fig.3.b.

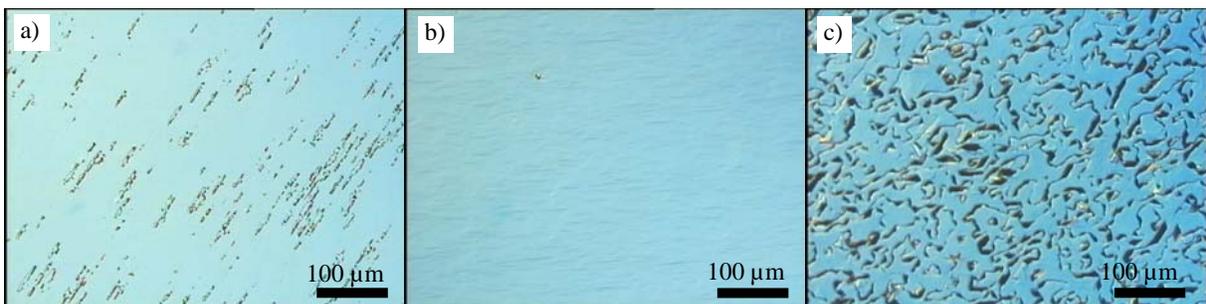


Fig.3: Nomarski images of 3C-SiC epilayers grown on 4H (0001) SiC substrates with the same growth conditions (1350 °C, C/Si = 1, Si/H₂ = 0.015 %). The C₃H₈ gas was introduced in the reactor chamber a) 0 min, b) 5 min and c) 15 min prior the SiH₄ gas (growth start). The epilayers are about 13 μm thick.

Growth rate. Typically growth rates used in this study were in the range 3 to 6 $\mu\text{m/h}$. As expected the growth rate increased with the temperature. However at 1350 $^{\circ}\text{C}$ and when a high flow of the C-precursor was added during the temperature ramp-up slight decreases of the growth rate was noticed (from typically 4.1 $\mu\text{m/h}$ to 3.7 $\mu\text{m/h}$).

Addition of N_2 gas. Since it was suggested that addition of nitrogen impurities could help to stabilize the 3C-SiC polytype when the growth conditions were not favoring the formation of 3C [14], all data reported here were obtained when adding a small N_2 gas during the growth process (typically $\text{N/C} = 0.3\%$). Moreover with the temperature ramp-up and growth conditions which gave the morphology shown in Fig.3.b, the removal of the N_2 gas flow during the growth did not influence the obtained morphology which confirms the above statement that close to ideal conditions were obtained for the growth process. The conductivity of this undoped layer was n-type and the net donor concentration was about $2 \times 10^{16} \text{ cm}^{-3}$ compared to the value of $5 \times 10^{16} \text{ cm}^{-3}$ when introducing the N_2 gas during growth. Using chloride based epitaxy [8] lower net carrier concentration has been achieved.

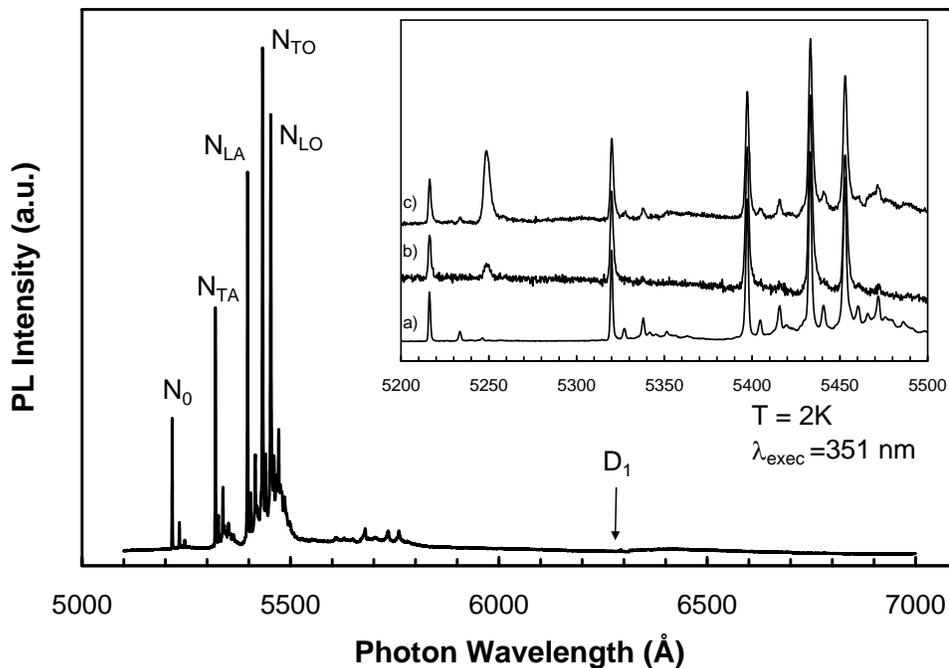


Fig. 4: Low temperature photoluminescence spectra of 3C grown layer. The large spectrum from a 4.5 μm thick layer and is near-band gap part is shown in the inset as a). The spectra b) and c) of the inset are recorded from a thin layer (2 μm) with two different excitation densities, respectively, where a new PL line is detected at about 5249 nm. The other sharp lines are multi bound excitons.

Characterization: AFM has been used to analyze the surface morphology of many epitaxial layers grown with the different process conditions as described before. However, attention has been put on epilayers showing smooth surface as that of Fig.3.b. A roughness (RMS, root mean square) of few nanometers (from 3 to 8 nm) was obtained over a 50 x 50 μm^2 area. This value decreased to less than 1 nm for 10 x 10 μm^2 area, however few steps with 5.5 nm high could be observed. Similar results were obtained when using the chloride based process [8]. Photoluminescence spectroscopy is a well recognized technique to access on the quality of the material [15, 16]. Typical photoluminescence spectrum recorded from those layers is presented in Fig.4. The spectrum is dominated by the near band gap emission which contains nitrogen bound-exciton (N-BE) related lines. Multi bound exciton lines are also observed. No donor-acceptor pair was observed, only weak signal coming from the D_1 center. The full width at half maximum of the transverse acoustic phonon of the N-BE has been proposed to be used to measure the N content in

3C material [15]. In Fig.4 (see inset) this width was about 1 meV for N₂ doped layer which should give an N concentration of 2x10¹⁶ cm⁻³; electrical measurement gave 5x10¹⁶ cm⁻³. For very thin layer (typically less than 2 μm) an additional line was observed at about 5249 Å with a width of 2 meV. The intensity of N-BE lines showed saturation at high excitation power density whereas this new line has a superlinear dependence under excitation, which could indicate a transition between nonradiative and radiative recombination regimes.

Summary

Growth of 3C-SiC epilayers on (0001) 4H-SiC is demonstrated using standard chemistry in a horizontal hot-wall reactor. Largely, single domain 3C epilayers were grown at a temperature of 1350 °C with a growth rate close to 4 μm/h and with a net doping concentration in the low 10¹⁶ cm⁻³ range. The important condition is the introduction of the C-precursor prior to the growth. The growth parameters window is however smaller than when using chloride-based CVD.

Acknowledgement

The Swedish Energy Agency, the Swedish Research Council and Tornbylyckorna-Lektorshagen at Linköping are gratefully acknowledged for financial support

References

- [1] D.F. Ferry, Phys. Rev. B 12 (1975) 2361-2369
- [2] W.E. Nelson, F.A. Halden, and A. Rosengreen; J. Appl. Phys. 37 (1966) 333-336
- [3] M. Soueidan, G. Ferro, O. Kim-Hak, F. Cauwet, B. Nsouli, Crystal Growth & Design 8 (2008) 1044-1050
- [4] V. Jokubavicius, R. Liljedahl, Y. Ou, H. Ou, S. Kamiyama, R. Yakimova, and M. Syväjärvi, Mat. Sc. For 679-680 (2011) 103-106
- [5] K. Nishino, T. Kimoto, H. Matsunami, Jpn. J. Appl. Phys. 36 (1997) 5202-5207
- [6] M. V. S. Chandrashekar, C. I. Thomas, J. Lu, M. G. Spencer, Appl. Phys. Lett. 90 (2007) 173509-1_173509-3
- [7] J. Lu, M.V.S. Chandrashekar, J.J. Parks, D.C. Ralph and M.G. Spencer, App. Phys. Lett. 94 (2009) 162115-1_162115-3
- [8] S. Leone, F.C. Beyer, A. Henry, O. Kordina and E. Janzén; Physica status solidi. Rapid research letters – 4 (11) (2010) 305-307
- [9] V.M. Polyakov and F. Schwiertz, J. Appl. Phys. 98 (2005) 023709-1_023709-6
- [10] A. A. Lebedev, A. M. Strel'chuk, N. S. Savkina, E. V. Bogdanova, A. S. Tregubova, A. N. Kuznetsov, and L. M. Sorokin, Techn. Phys. Lett., 28 (2002) 1011–1014.
- [11] S. Nishino, J. A. Powell, and H. A. Will, Appl. Phys. Lett. 42 (1983) 460-463
- [12] S. Roy, M. Portail, T. Chassagne, J. M. Chauveau, P. Vennéguès and M. Zielinski, Appl. Phys. Lett. 95 (2009) 081903
- [13] S. Leone, F.C. Beyer, A. Henry, O. Kordina and E. Janzén, AIP Conference Proceedings 1292 (2010) 7-10.
- [14] G. Ferro, Mater. Sci. Forum 645–648 (2010) 49-54
- [15] J. Camassel, S. Juillaguet, M. Zielinski, and C. Balloud, Chem. Vap. Dep. 12 (2006) 549
- [16] G. Zoulis, J. Sun, R. Vasiliauskas, J. Lorenzini, H. Peyre, M. Syväjärvi, G. Ferro, S. Juillaguet, R. Yakimova and J. Camassel, this proceeding