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

Original Publication:

Xun Li, Henrik Jacobson, Alexandre Boulle, Didier Chaussende and Anne Henry, Double-Position-Boundaries Free 3C-SiC Epitaxial Layers Grown on On-Axis 4H-SiC, 2014, ECS Journal of Solid State Science and Technology, (3), 4, P75-P81.

http://dx.doi.org/10.1149/2.012404jss

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Postprint available at: Linköping University Electronic Press

http://urn.kb.se/resolve?urn=urn:nbn:se:liu:diva-106298

Double-position-boundaries free 3C-SiC epitaxial layers grown on on-axis 4H-SiC

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ABSTRACT

High quality double-position-boundaries free 3C-SiC epilayers have been successfully grown on on-axis (0001) 4H-SiC by chemical vapor deposition at optimized conditions as observed with optical microscopy and X-ray diffraction. The effect of the growth parameters, including temperature, C/Si ratio, ramp-up condition, Si/H_2 ratio, N_2 addition and pressure, on the quality of the grown layers is investigated. Different techniques, including microscopic and spectroscopic techniques, are used to characterize the epilayers. High resolution X-ray diffraction shows 2θ-ω curve with full width at half maximum of only 16 arcsec for the (111) reflection detected from a 35 μm thick 3C-SiC layer, showing the good structural quality of the layer. Reciprocal space maps confirm the absence of double-position-boundaries in a large depth of the layers. Low temperature photoluminescence measurement shows clear near-band gap emission with sharp and single peaks, which further verifies the high quality of the epilayers.

I Introduction

Among the most common SiC polytypes, 3C-SiC is the only one with a cubic structure; it is thus an extremely interesting material for fundamental solid-state physics investigations and of exceptional potential for various applications. Its superior properties over the other SiC polytypes and other semiconductors are high electron mobility[1], good electron drift velocity[2] and lower interface trap density with oxide[3], which will be beneficial for MOSFET and HEMT devices. It can also be used for MEMS application due to its hardness[4].

The growth of 3C-SiC on Si substrates by chemical vapor deposition (CVD) has been studied intensively since last century due to Si wafers combining both low cost and large diameters. In addition, the direct use of standard silicon processing lines would be possible. However, this approach has shown its own limitation due to the big mismatches of both materials, Si and 3C-SiC, in thermal expansion coefficients (8%) and lattice constants (20%). The obtained 3C-SiC epilayers have poor crystalline quality and encounter a very high density of defects, such as voids, stacking faults and anti-phase domains, which appeared as incompatible with any electronic device. Most of the work has been conducted on (001) Si substrates leading to (001) 3C-SiC layers. The (111) oriented 3C-SiC, which is a suitable substrate for hexagonal nitrides growth, has severe cracking and warping problems when grown on (111) Si substrate compared to the (001) oriented heteroepitaxial system[5]. Experimental works using other orientations and/or off-cut substrates have also been reported. For instance, a decrease of the stacking faults density has been noted when using (211) Si substrate on which 3C-SiC crystal can grow with a step-flow mode[6]. Using α-SiC substrates, growth of higher quality 3C epilayers could be achieved not only by CVD[7,8], but also by continuous-feed physical vapor transport (CF-PVT)[9], vapor-liquid-solid (VLS)[10], top-seeded solution growth technique (TSSG)[11] and sublimation epitaxy technique[12]. However, the

defect called double positioning boundary (DPB), a particular case of twin boundary, is present when using α-SiC substrates. This is mainly due to the fact that 3C has two types of stacking sequence with a 60° rotation difference (i.e. ACB and ABC) when grown on the basal plane of a hexagonal polytype.

The elimination of DPBs has been studied by many groups. 3C layers grown on low-tilt-angle vicinal Si-face 6H substrates by CVD have been found to contain less DPBs than those on C-face[13]. Soueidan et al.[14] have successfully grown DPBs free 3C-SiC layers on on-axis Si-face 4H and 6H substrates and also on 3.5° off Si-face 6H substrates using VLS methods with Si-Ge melts, however, reproducibility issues are mentioned. Using substrates as 4°, 8° off Si-face 4H or on-axis C-face 6H, 3C epilayers with DBPs are always obtained. Less DPBs were shown to emerge for epilayers grown on 15R substrates compared with films grown on 6H-SiC[15,16]. The growth of DPBs-free 3C-SiC on patterned 4H substrates, using both VLS[17] and CVD[18], has also been reported. However, this method needs precise lithography and dry etching technique for substrate preparation and only small area free of DPBs are obtained, typically around 200 x 200 μm^2. Using TSSG technique DPBs-free 3C layers were obtained only on 6H-SiC 4º off-cut oriented toward the [1-100] direction[11]. The model discussed for the elimination of DPB is based on anisotropic lateral expansion of the two 3C domains and was first proposed by Latu-Romain et al.[19]. More recently using Monte-Carlo simulations, the possibility to obtain DPBs-free 3C epilayers has been predicted only on misoriented 6H substrates with large miscut (~ 8º was proposed but towards [11-20]), for on-axis substrates (both 6H and 4H) a random distribution of large 3C-SiC domains should appear and for the growth on 4H-SiC substrates with large miscut, dislocations would degrade the layer quality[20]. It is worth noting that the largest sample free of DPB reported to date has been obtained by the CF-PVT method and is a 30 mm diameter free-standing (111) 3C-SiC

layer grown on an on-axis substrate[21]. Again, serious reproducibility problems are mentioned. To our knowledge, all the reported attempts to grow DPB-free epilayers by standard CVD have always been unsuccessful.

In this paper, we report the CVD growth of high quality 3C-SiC epilayers on 4H-SiC nominally on-axis substrates with large single domain area. The experimental procedures are described in Section II. Results regarding the effect of various growth parameters on the morphology of the obtained layers are displayed in Section III. Section IV gives more detailed characterization information and in section V a discussion and a tentative description of the growth process are presented.

II Experimental

All the 3C-SiC epilayers were grown in a horizontal hot-wall CVD reactor without rotation and with standard chemistry using silane (SiH_4) and propane (C_3H_8) as precursors. The substrates are commercial n-type doped on-axis 4H-SiC (0001) with unintentional tilt angle of less than 0.08° as specified by the supplier. All the samples, which have been cut into the size of about 2x2 cm^2, are from wafers in the same boule. Si-face is chosen for this study in order to get lower net doping concentration in the grown layer. Hydrogen and argon (5% of Ar in H_2) were used as carrier gases. All the growth runs began with a heating procedure from room temperature to a certain stabilization temperature and then stayed at this temperature for 10 min[22]. This stabilization temperature was generally set at 1250 °C, but could be slightly lower depending on the growth temperature. Then the susceptor was further heated to the growth temperature. A reduced process pressure, typically 200 mbar, was used.

At the early stage of our experiments, a small amount of nitrogen gas (N/C = 0.32%) was always added into the chamber during the growth procedure. The introduction of N_2 has been always prior that of SiH_4. This was due to a previously reported work[23]: adding N_2 impurities could increase C vacancies and help to stabilize cubic polytype. This is especially useful when the conditions are not suitable for the 3C-SiC growth. The optimization of several process parameters (temperature, C/Si ratio, ramp-up condition and pressure) is presented in this work. Reproducibility of the results has not been tried when the growth conditions were not optimized. However, when the process parameters are well defined and controlled to achieved DPB free layers, results could have been repeated for at least three times.

The morphology and surface roughness of the layers were investigated by Nomarski differential interference contrast (NDIC) optical microscopy and tapping mode atomic force microscopy (AFM). The crystalline quality of the grown epilayers was analyzed by (1) low temperature photoluminescence (LTPL) at 2K in a bath cryostat using 351 nm Ar^+ laser line for excitation; (2) high resolution X-ray diffraction (HRXRD). Triple-axis measurements were employed to ω rocking curves and 2θ-ω diffraction curves. On the primary side a Ge (220) crystal monochromator was used. The secondary side had a Ge (220) triple-bounce collimator crystal that limits the acceptance into the detector to less than 12 arcsec; (3) electron back scattering diffraction (EBSD). The thickness of the 3C-SiC layers was measured by Fourier Transform Infrared (FTIR) reflectance. The net doping concentration was determined by Hg probe capacitance-voltage (CV) method at room temperature.

III Growth results and discussion

The growth temperature and C/Si ratio are probably the two most important process parameters which are influencing the growth process and therefore the results. They are also closely related to each other since the decomposition of SiH_4 and C_3H_8 are temperature dependent. Their effect on the morphology and crystalline quality of the obtained films is presented here. Then the surface preparation of the substrate either during temperature ramp-up or at the growth temperature but prior to the growth is reported. The growth rate effect on the crystal quality of the layer is also investigated. Results from growth done at various pressures are also described. Finally, comparison when using (0001) 6H-SiC as substrate is presented.

III.1. Temperature effect

The growth temperature was varied between 1200 °C and 1400 °C using the same C-rich ramp-up conditions. Figure 1 shows the surface morphology of 3C epilayers grown with a fixed pressure of 200 mbar, C/Si = 1, Si/H_2 = 0.02% and N/C = 0.32%. When the temperature is 1325 °C or even lower, the surface of the layers appears very dark as shown in Fig. 1a. The deposit, analyzed by µ-Raman shows only strong signal associated to both Si and 3C-SiC. No carbon related peak could be observed. Further XRD measurement reveals polycrystalline structure for both Si and 3C-SiC. A temperature of 1350 °C is found to be the most favorable one to grow uniform layer without any DPBs (Fig. 1b). At higher growth temperature, typically 1375 °C some small DPBs are observed (Fig. 1c) giving rise to a global surface morphology degradation when the temperature is further increased (Fig. 1d). Note that the growth rates are respectively of 4.9 µm/h, 5.9 µm/h and 5.6 µm/h for a temperature of 1350 °C, 1375 °C and 1400°C. For this latter temperature of 1400°C,

decreasing the Si/H_2 ratio from 0.02% to 0.015% decreases the growth rate to 4.7 μm/h as expected, but the layer still remains polycrystalline.

III.2. C/Si ratio effect

At the growth temperature of 1350 ºC, good surface morphology of the 3C layers could be obtained only when using a C/Si ratio in a narrow range close to 1. With Si-rich conditions (C/Si ≤ 0.9), silicon condenses on the SiC surface, forming Si hillocks which look like solidified Si droplets. Such hillocks are shown in Fig. 2a, from a sample grown at 1350 ºC, with C/Si = 0.9, Si/H_2 = 0.022%. After wet chemical etching in a HNO_3: HF: CH_3COOH (5:3:3) solution, most of the Si hillocks vanished (Fig. 2c). The remaining surface is relatively smooth. No crater or depth perturbation of the surface was revealed which would suggest that the Si clusters are present only on the top surface of the layer, not through the epilayer. Note that the silane flux is switched off before cooling down. For C-rich conditions (C/Si>1.1), the quality of the epilayers degrades compared to when using a C/Si = 1 (see Figure 2b in comparison with Fig. 1b). The surface is very rough and DPBs and other types of defect appear on the surface.

III.3. Temperature ramp-up conditions

When both precursors SiH_4 and C_3H_8 were introduced directly at the growth temperature, DPBs were always observed. Si-rich condition during temperature ramp-up or prior the growth was not tested since it is known to stabilize the 4H polytype for the growth on nominally on-axis 4H-SiC substrate, but at a much higher temperature than used in this study[24,25]. Thus, two different temperature ramp-up conditions have been tested. All these ramp-up conditions are followed by the same growth step, experiments were done at 200 mbar, 1350 °C, C/Si = 1, Si/H_2 = 0.015%.

The growth time differs from one experiment to another and is comprised between 1 h and 4 h, the growth rate of 4 µm/h being similar.

- In the first case, the C_3H_8 precursor was introduced into the reactor from room temperature. Once the growth temperature was reached, the C_3H_8 flow was set to the growth flow before the introduction of SiH_4 in the gas mixture. During this first step of heating up, various C_3H_8 flows were tested (Fig. 3). Without C_3H_8 flow or if the flow is too small compared to the growth flow, the morphology of the layer is characterized by a high density of DPBs. If the same flow is used during temperature ramp-up and growth, the grown 3C-SiC epilayers are single domain (Fig. 3a). But if the flow is too high (typically higher than the growth flow), the material quality is degraded and many defects are observed (Fig. 3b). With further increasing of the C_3H_8 flow to the maximum allowed by the system, the sample surface is again covered by DPBs (Fig. 3c).
- In the second case, surface preparation in C-rich atmosphere was investigated by having a C_3H_8 flow through the susceptor at the growth temperature before introducing SiH_4. In this case, the temperature ramp-up is performed under H_2 ambient (with 5% Ar) and once the growth temperature is reached, a 0.015% C_3H_8 in H_2 treatment is conducted prior the growth with varying times: 0 min, 5 min, and 15 min (Fig. 3d-f). As already mentioned, many DPBs were observed when the growth started directly after the heating stage, i.e. for a C-rich treatment time of 0 min (Fig. 3d). After a 5 min treatment only, the epilayer surface exhibits a smooth morphology without any DPB (Fig. 3e). The observed stripe features are usually related to the emergence of stacking faults to the surface. For a longer treatment time (15 min), the epilayer contains a high density of DPBs (Fig. 3f).

III.4. Growth rate

A set of experiments was carried out to study the influence of the average growth rate on the occurrence of DPB-free layers. As expected, the growth rate almost linearly increases with the Si/H_2 ratio (Fig. 4), when keeping the other growth parameters constant. According to the trend given by the fit line, the growth rate has a negative value when $Si/H_2 = 0$ corresponding to a small etching rate by hydrogen of 0.02 µm/h. When the Si/H_2 ratio is below 0.019%, the surface of the 3C-SiC layers is basically as good as shown in Fig. 1b or 3e, i.e. with single domain layer, only if one of the correct ramp-up conditions is applied. When using higher Si/H_2 ratio, either a high density of Si hillocks was observed on the layer surface or the epilayer has a polycrystalline structure.

III.5. Pressure effect

Different process pressures, from 200 mbar up to 500 mbar, have also been investigated, keeping the other growth parameters similar i.e. 1350°C, with C/Si = 1 and $Si/H_2 = 0.015\%$. The growth rates are almost the same considering the measurement deviation, about 4.5 µm/h for 300 mbar and 500 mbar, 4.6 µm/h for 400 mbar. These values are slightly higher compared to the growth rate obtained at 200 mbar (4.2 µm/h). This is supposed to be due to an enhanced etching at low pressure which reduces slightly the growth rate. The layers grown at a pressure higher than 200 mbar were not totally single domain, however very large single domains (more than 200x200 μm^2) have been observed with the optical microscopy. Effect of pressure has not been studied much deeper but according to the results obtained, DPB-free layers should also be obtained by slightly tuning the working conditions. Nevertheless, the hydrogen etching, which is more important at

lower pressure, could favor the preparation of the surface for optimal growth. And a low pressure (typically of 200 mbar) gave pretty good results.

III.6. Comparison with 3C on 6H

The growth of 3C-SiC on on-axis Si-face 6H-SiC substrates has been done in the same CVD reactor using the optimized process for DPB free 3C-SiC epilayer on 4H-SiC as a starting point. Different morphology was observed and results were generally not as good as for epilayers grown on 4H substrates (the sample in Fig. 5 was grown at 1350 °C, 200 mbar, C/Si = 1, Si/H_2 = 0.015% and with moderate C-rich ramp-up condition). The epilayer is 100% 3C but with some DBPs and triangular defects. When the growth temperature is decreased to 1325 °C, Si hillocks are observed on the layer surface. While increasing the temperature to 1375 °C, the epilayer is found to have only about 40% 3C, meaning that homo-epitaxy (6H on 6H) appears for the other 60% of the surface. At 1400 °C, almost 100% 6H was epitaxially grown. As in the case when using nominally on-axis 4H-SiC substrates, epilayers grown with low C/Si ($\leq$ 0.9) have a top surface covered by Si clusters, whereas epilayers grown with high C/Si ($\geq$ 1.3) have a polycrystalline structure. Surface preparation with C rich ambient prior the growth is also found a necessary condition to stabilize the 3C polytype and obtain large domains as observed in Fig. 5.

IV Detailed characterization

IV.1. Further morphology characterization with AFM

Figure 6a shows an image of a typical boundary between two domains for a 20 µm thick epilayer. This boundary is actually a shallow groove and depending on the location on the sample, the

groove depth varies from 45 nm to 87 nm for a 20 μm thick epilayer and could be as deep as 120 nm for thicker layers. The surface roughness of the smoother samples as shown in Fig. 3e is typically between 3 and 8 nm (RMS value) over a 50x50 μm^2 area. When applied to a small area of 10x10 μm^2, it decreases to less than 1 nm (Fig. 6b). On this AFM picture, stripe features similar to those observed with optical image (Fig. 3e) are also observed. The highest step measured on this sample surface is less than 5.5 nm. The visualization of these stripe features is further enhanced after KOH etching (Fig. 6c) and well defined triangular shapes can be observed which are associated to stacking faults. From this picture staking faults density can be determined, typically in the $2{\cdot}10^4$ to $5{\cdot}10^4$ cm^{-1} range.

IV.2. Structural analysis

As already mentioned, Figure 3e shows a typical surface morphology of a DPB-free sample. EBSD measurement, which is based on weak diffraction pattern and shows orientation and phase of the crystal, was applied to almost the whole sample. The scan confirmed that there is only one 3C domain for this layer. With statistical treatments, the confidence index was calculated to be close to 100% with the exception of the position close to one downfall particle. However it should be noted that the penetration depth of EBSD technique is only a few tens of nanometers. So this technique can be seen as a surface technique and further investigations should be done to access more information on the complete layer and not only top surface.

In order to further evaluate the structure quality of the 3C layer more deeply, HRXRD was performed. Reciprocal space maps (RSM) of either the (113) or (111) reflection have confirmed the absence of DPB in a large depth of our 3C-SiC layers. As an example for the sample with thickness of 12.5 μm (same as Fig. 3e), the percentage of the presence of a second domain was

evaluated to be less than 0.1%. This is determined from the intensity recorded from the (113) reflection peak or RSM map as shown in Fig. 7a and 7b. When rotating the sample with 60º around its symmetry axis the intensity of the diffraction changes from maximal value to almost zero. We should notice here that the penetration depth (with the 1/e attenuation criterion) of the X-rays for the (113) reflection is about 8 μm. We could thus expect that either the layer was with single domain from the interface layer/substrate (3C/4H), or due to the growth mechanism less than 5 μm are needed to convert layer containing DPB to single domain layer. However, with RSM of the (111) reflection peak as shown in Fig. 7c no symmetry is observed around the [111] direction. This confirms in this case that the DPB free layer can be obtained directly from the nucleation stage meaning at the interface layer/substrate since the penetration of the X-rays is 22 μm for this direction. In the RSM of the (111) peak, additional features (diffuse streaks) associated to stacking faults are also visualized; they correspond to SFs lying in the (-111) plane (for the streak with an angle of 70º) and stacking faults lying in the (11-1) and (1-11) planes (for the streak with an angle of 55º). The stacking faults density can be evaluated from the intensity of these streaks[26] and is found to be in the 1-2x10^4 cm^{-1} range.

Figure 8a is a typical 2θ-ω curve collected from (111) Bragg reflection for a 35 μm thick 3C-SiC epilayer. As mentioned the penetration depth of the X-rays is expected to be 22 μm at this reflection and the footprint size used in the measurement is typically 1x1.7 mm^2. The reflection peak has a full width at half maximum (FWHM) of 16 arcsec. For the relatively thick layer, this indicates that the strain along the c-axis is low in the 22 μm top layer. FWHM values of rocking curves reported in the literature are generally very high for 3C layers grown on 6H substrates with few hundred of arcsec[27], to the best of our knowledge. Recently, a value of 32 arcsec of the (111) reflection peak was reported for a 760 μm thick 3C layer, which was grown on a low off-cut angle 6H substrate[28].

In addition a FWHM value of 78 arcsec has been measured for the (002) reflection rocking curve from thick 3C-SiC freestanding layers grown by sublimation method using CVD-grown 3C seeds[29]. We observe similar FWHM value (72 arcsec) for our 35 µm 3C-SiC epilayer (Fig. 8b), however, this (002) reflection spectrum consists of an overlapping of many sharp peaks with FWHM of only few arcsec. A few of the observed peaks with low intensity and random pattern on the both sides of the more intense peaks could be related to noise. But the stronger and sharper peaks are definitively not noise due to their intensity is much higher than the square root of the total intensity. From this observation, sub-domains, which are with the same stacking sequence, are proposed to exist between the staking faults observed with optical microscopy and AFM. The sub-domains are slightly tilted one to each other with angles in the 0.003 to 0.02 degrees range. As their FWHM is extremely small (less than 5 arcsec) their crystalline quality is extremely high. The ω curves reported in the literature are generally smooth which could be due to either lower resolution during the experiments, or due to bending of the layer or mosaicity which results to a broadening of the ω peak. The lowest FWHMs reported for our samples are additional proofs of the high quality of the layer.

IV.3. Electrical and optical properties

The net donor concentration is about 5×10^{16} cm^{-3} for most of the slightly doped samples with N/C = 0.32% as measured by CV measurements at room temperature. For the undoped samples, the doping concentration could decrease to 2×10^{16} cm^{-3}. This residual doping level is comparable to those obtained when 3C-SiC layers are grown on Si substrate[30]. Using chloride-based chemistry for the growth[7], the net carrier concentration of 3C-SiC layers grown on 6H-SiC substrate could

achieve mid 10^{15} cm^{-3}. This lowest residual doping is probably due to higher growth rate, typically 10 µm/h obtained with chloride based chemistry.

LTPL has been performed at 2K on many samples using excitation of the 351 nm Ar^+ laser line. Figure 9 shows the spectrum of the sample for which the morphology is presented in Figure 3a. This extended spectrum is representative for all undoped and slightly doped layers investigated. According to the measurement done on many locations as a mapping, the layer is 100% 3C-SiC. The PL spectrum is dominated by the near-band gap emission (520-550 nm; 2.4-2.2 eV), which contains the nitrogen bound exciton (N-BE) and its phonons replica as well as multi bound exciton lines. Free-exciton related lines have been observed only for the undoped layers. The two phonons replica region is observed around 2.17 eV. A weak signal related to D_1 center was recorded at 1.97 eV (628.7 nm). We observed this line for all the investigated samples with a full width at half maximum (FWHM) of about 1 meV. Its energy position was slightly shifted from sample to sample between 1.9726 eV for 52 µm thick layer to 1.9700 eV for the thinner layer (4 µm thick). No donor-acceptor pair recombination is observed in this extended spectrum (Fig. 9) as well as in all spectra recorded from other layers. The nitrogen concentration is in the range of low 10^{16} cm^{-3} by measuring the FWHM of the N-BE transverse acoustic phonon (N_{TA})[31], doping which also explains why the free-exciton luminescence is rarely observed. The inset of the figure shows the N-BE no-phonon line (N_0) for three different 3C epilayers having different thicknesses as well as for a bulk pure single-crystal 3C-SiC grown with CF-PVT[19]. For the bulk sample the N_0 line is extremely narrow (FWHM = 0.4 meV) which corresponds to the spectral resolution limit of PL equipment at this wavelength. Its energy position at 2.3784 eV is very close to the value reported for bulk 3C-SiC crystal grown by the Lely technique[32]. For our CVD layer the FWHM of the N_0 lines is slightly larger with a value of 1.3 meV for the 12 µm thick layer. Note that those layers

were grown with slightly different growth conditions (lower growth rate for the thinner layer) and all with small amount of nitrogen in the gas mixture. For the thicker layer, this no-phonon line is observed at 2.378 eV very close to the bulk value. For the thinner layers, this no-phonon line slightly shifts from the expected position towards low energy. The same energy shift is observed for the phonon replica without discrepancy. Note that for the thinner layer (4 µm thick) this shift is only of 2 meV towards lower energy compared to the thicker layer. Shifts of 7 meV are typically reported in the literature for 5 µm thick 3C-SiC epilayer grown on Si substrate[33] and the width of the N_0 line close to 2 meV[34]. The shift is an indication of the internal stress in the layer and the broadening could be related to high doping concentration. Another indication of the stress in 3C epilayer is given by the relative intensity of the N-BE no-phonon (N_0), TA, LA and LO lines with respect to the TO line. In stressed epilayer the N_0 is seldom observed. Table I lists the corresponding data for three experimental samples of Fig. 9.

V Discussion

From all the experiments, there are apparently two critical issues for obtaining DPB-free 3C-SiC heteroepitaxial layers on (0001) on-axis 4H-SiC substrates:

- A very narrow operating window. Typical growth conditions are 1350°C and a C/Si ratio of 1 for a pressure of 200 mbar. Even slight variations from those conditions can give rise to DPB formation.
- Specific ramp-up conditions. A carbon-rich surface preparation, either during heating-up or prior to the growth at growth temperature is essential to get DPB-free epilayer.

In all epilayer deposition processes, in-situ surface preparation prior to the growth is essential as it governs the nucleation of the layer and consequently its quality. It is thus not surprising that for SiC growth, especially for CVD deposition the in-situ surface preparation is still the topic in many studies. The problem of DPBs reduction has already been tackled, using for instance HCl for the in-situ preparation of on-axis 6H-SiC substrates[35]. (0001) SiC surface reconstructions have been studied intensively and among the important conclusions, Starke et al.[36] have shown that during the formation of the (√3X√3)-R30º on hexagonal (0001) SiC, Si rich conditions should promote a cubic sequence to develop at 1000 ºC. But this is in apparent contradiction with our observation which evidences that C-rich conditions prior the growth are required to promote high quality 3C-SiC growth. This puzzling result has to be discussed further.

The experiment presented in Figure 1a shows that at 1325°C, i.e. only 25°C below the optimal temperature of 1350°C, a SiC+Si deposit forms on the substrate. This suggests that the gas phase has a silicon excess if the temperature decreases. On the other hand, we observed Si clusters on the sample surface at 1350°C when the Si/H_2 ratio is increased (Fig. 2a). After removal of the Si hillocks by wet chemical etching, we found no deep depression below and the whole SiC surface was smooth. As the growth was not affected by the presence of these Si clusters, they probably form after the growth during the cooling stage of the reactor (cooling rate is around 20 ºC/min) although the silane flux was switched-off. They also can be formed during the growth, however, they may not necessarily affect or stop the growth and contrarily could promote the growth.

The conclusions from these observations are twofold. First, our optimal 3C-SiC deposition conditions are Si-rich and very close to Si condensation in the film. Secondly, there is an additional silicon source in the reactor, even if no silane flux is used. The only reasonable source of silicon is the susceptor itself; large area of the susceptor upstream is loaded with silicon during every

growth experiments (because the 3C-SiC experiments are conducted at low temperature, typically 1350°C which is much lower than the typical temperatures used for 4H-SiC homoepitaxy). During the temperature ramp-up prior the growth, this extra silicon is vaporized and acts as a Si source. Differently said, the so-called C-rich treatment before the growth (either during ramp-up or at the growth temperature) is actually the nucleation and the growth of a first 3C-SiC layer on the 4H-SiC substrate. For clarity purpose, we will call this first layer "buffer layer" as it governs the occurrence or not of DPBs. At this stage, the conditions of formation of such buffer layer are not clear as the silicon flux coming from the vaporization of a silicon excess upstream is unknown. Nevertheless, some information can be extracted from the experiments.

- The growth rate of this buffer layer is independent on the propane flow rate as the samples of Fig. 3a-c have exactly the same thickness of 15 µm. The silicon source flux is thus limiting the growth kinetics.
- This buffer layer already forms at lower temperature because the sample of Fig. 3a prepared with propane introduced from room temperature is also free of DPB.
- The propane treatment time at growth temperature is important. Without treatment (Fig. 3d), there is no buffer layer and the layer has many DPBs. After 15 min (Fig. 3e), many DPBs are observed whereas no DPBs are present after only 5 minutes. The buffer layer thus degrades after a while, probably indicating that the Si load consumption could affect the stoichiometry in the gas phase.

At the low temperatures used in this study, it is not surprising to get nucleation of 3C-SiC. However, it is not clear from the present data why single domain layers can be obtained directly from the nucleation. Additional information as cross sectional observation, would be needed to investigate more in detail the interface 3C/4H, especially in the case of our 12.5 µm thick epilayers

(Fig. 3e, Fig. 7). This is anyway an extreme case. Generally for our thin layers (less than 3 µm) DPBs are observed whereas for thicker layers (more than 3 µm thick) DPB free surface is observed. This leads to the discussion regarding lateral growth, where one type of domains can easily over grow the other. Bending of boundaries has been proposed which could depend on the domains size and/or to the lateral (or in-plane) growth rate[37]. High lateral growth rate in specific directions should be applied, which will allow two domains with the same stacking sequence (e.g. ABCABC) to cover a domain characterized with the other stacking sequence (ACBACB). When this occurs stacking fault would be expected at the intersection and this mechanism would give rise to sub-domains having the same stacking sequence but slightly mis-oriented or tilted for each other from the [111] direction. These sub-domains are revealed here with the HRXRD (see section IV.3) for the first time, to the best of our knowledge.

VI Summary

In this paper, the growth process and detailed characterization of 3C epilayer on 4H substrates are studied. We have demonstrated that DPB-free epilayers could be obtained on a large dimension (2x2 cm^2) with a standard SiH_4+C_3H_8+H_2 CVD chemistry and without any use of chlorine. It has been found out that a critical point to get DPB-free layer is the occurrence of a buffer layer prior to the growth, formed without any silane injected but using a silicon excess already present in the susceptor. The condition of formation of such buffer layer is unclear and would require specific works. Finally, a thorough characterization of the DPB-free layer is presented. We pointed out the high quality of the 3C layer. The highest growth rate is up to 5 µm/h for achieving smooth layers with RMS value <1 nm for 10x10 μm^2 area. The high purity of the layers is confirmed with PL

and the lowest net doping concentration is about $2x10^{16}$ cm^{-3}. The FWHM obtained from HRXRD 2 theta omega curve for a 35 µm 3C layer of the (111) reflection was only 26 arcsec, which denotes high crystal quality material. From the (002) reflection rocking curve, existence of sub-domains is proposed, which could be at the origin of stacking faults observed on the surface of the layers.

Acknowledgements

Financial support from the Swedish Energy Agency (project 32917-1) is gratefully acknowledged. Mr. Patrick Chaudouet is acknowledged for EBSD measurements and Dr. Ivan Ivanov for assistance in the µ-Raman measurements.

References

1. D. F. Ferry, *Phys. Rev. B*, **12**, 2361 (1975).

2. W. E. Nelson, F. A. Halden, and A. Rosengreen, *J. Appl. Phys.,* **37**, 333 (1966).

3. A. Schöner, M. Krieger, G. Pensl, M. Abe, and H. Nagasawa, *Chem. Vap. Deposition*, **12**, 523 (2006).

4. R. Cheung, *Silicon Carbide Micro Electromechanical Systems for Harsh Environments*, Imperial College Press (2006).

5. H. P. Liaw and R. F. Davis, *J. Electrochem. Soc.,* **131**, 3014 (1984).

6. T. Nishiguchi, Y. Mukai, M. Nakamura, K. Nishio, T. Isshiki, S. Ohshima, and S. Nishino, *Mat. Sci. Forum,* **457-460**, 285 (2004).

7. S. Leone, F. C. Beyer, A. Henry, O. Kordina, and E. Janzén, *Phys. Status Solidi RRL,* **4**, 305 (2010).

8. J. A. Powell, J. B. Petit, J. H. Edgar, I. G. Jenkins, L. G. Matus, J. W. Yang, P. Pirouz, W. J. Choyke, L. Clemen, and M. Yoganathan, *Appl. Phys. Lett.*, **59**, 333 (1991).

9. L. Latu-Romain, D. Chaussende, C. Balloud, S. Juillaguet, L. Rapenne, E. Pernot, J. Camassel, M. Pons, and R. Madar, *Mat. Sci. Forum,* **527-529**, 99 (2006).

10. M. Soueidan and G. Ferro, *Adv. Funct. Mater.,* **16**, 975 (2006).

11. K. Seki, S. Harada, and T. Ujihara, *Mat. Sci. Forum,* **740-742**, 311 (2013).

12. A. A. Lebedev, V. V Zelenin., P. L. Abramov, E. V. Bogdanova, S. P. Lebedev, D. K. Nel'son, B. S. Razbirin, M. P. Shcheglov, A. S. Tregubova, M. Suvajarvi, and R. Yakimova, *Semiconductors,* **41**, 263 (2007).

13. H. S. Kong, J. T. Glass, and R. F. Davis, *J. Mater. Res.*, **4**, 204 (1989).

14. M. Soueidan, G. Ferro, O. Kim-Hak, F. Cauwet, and B. Nsouli, *Cryst. Growth Des.,* **8**, 1044 (2008).

15. K. Nishino, T. Kimoto, and H. Matsunami, *Jpn. J. Appl. Phys.,* **36**, 5202 (1997).

16. F-R. Chen, S. R. Nutt, W. S. Yoo, T. Kimoto, and H. Matsunami, *J. Cryst. Growth*, **137**, 175 (1994).

17. J. Lorenzzi, M. Lazar, D. Tournier, N. Jegenyes, D. Carole, F. Cauwet, and G. Ferro, *Cryst. Growth Des.,* **11**, 2177 (2011).

18. P. G. Neudeck, A. J. Trunek, D. J Spry, J. A. Powell, H. Du, M. Skowronski, X. R. Huang, and M. Dudley, *Chem. Vap. Deposition,* **12**, 531 (2006).

19. L. Latu-Romain, D. Chaussende, and M. Pons, *Cryst. Growth Des.*, **6**, 2788 (2006).

20. M. Camarda, A. La Magna, and F. La Via, *Mat. Sci. Forum,* **740-742**, 295 (2013).

21. D. Chaussende, L. Latu-Romain, L. Auvray, M. Ucar, M. Pons, and R. Madar, *Mat. Sci. Forum*, **483-485**, 225 (2005).

22. A. Henry, J. ul Hassan, J. P. Bergman, C. Hallin, and E. Janzén, *Chem. Vap. Deposition,* **12,** 475 (2006).

23. G. Ferro, *Mater. Sci. Forum,* **645–648**, 49 (2010).

24. S. Leone, F. C. Beyer, H. Pederson, O. Kordina, A. Henry, and E. Janzén, *Cryst. Growth Des.,* **10**, 5334 (2010).

25. J. Hassan, J. P. Bergman, A. Henry, and Janzén, *J. Cryst. Growth,* **310**, 4424 (2008).

26. A. Boulle, D. Chaussende, F. Conchon, G. Ferro, and O. Masson, *J. Cryst. Growth,* **310**, 982 (2008).

27. R. Vasiliauskas, S. Juillaguet, M. Syväjärvi, and R. Yakimova, *J. Cryst. Growth,* **348**, 91 (2012).

28. J. W. Sun, I. G. Ivanov, R. Liljedahl, R.Yakimova, and M. Syväjärvi, *Appl. Phys. Lett.,***100**, 252101 (2012).

29. P. Hens, V. Jokubavicius, R. Liljedahl, G. Wagner, R. Yakimova, P. Wellmann, and M. Syväjärvi, *Materials Letters,* **67**, 300 (2012).

30. M. Zielinski, M. Portail, H. Peyre, T. Chassagne, S. Ndiaye, B. Boyer, A. Leycuras, and J. Camassel, *Mat. Sci. Forum,* **556-557**, 207 (2007).

31. J. Camassel, S. Juillaguet, M. Zielinski, and C. Balloud, *Chem. Vap. Deposition,* **12**, 549 (2006).

32. W. J. Choyke, D. R. Hamilton, and L. Patrick, *Phys. Rev*., **133**, A1163 (1964).

33. W. J. Choyke, Z. C. Feng, and J. A. Powell, *J. Appl. Phys.,* **64**, 3163 (1988).

34. S. G. Bishop and J. A. Freitas Jr., *J. Cryst. Growth*, **106**, 38 (1990).

35. Z. Y. Xie, J. H. Edgar, B. K. Burkland, J. T. George, and J. Chaudhuri, *J. Cryst.Growth,* **224**, 235 (2001).

36. U. Starke, J. Schardt, J. Bernhardt, M. Franke, and K. Heinz, *Phys. Rev. Lett.,* **82**, 2107 (1999).

37. F. La Via, *Silicon Carbide Epitaxy*, chapter 9, IBSN:978-81-308-0500-9 (2012).

Table I. The intensity ratio (in %) of the N-BE lines to the TO phonon replicas lines for three 3C-SiC epilayers with different thickness t and for the bulk 3C sample. The shifts of the line position with respect to that of the bulk 3C sample ΔE is given in meV.

Sample	t (μm)	I_0/I_{TO}	I_{TA}/I_{TO}	I_{LA}/I_{TO}	I_{LO}/I_{TO}	ΔE (meV)
1	4	20	41	67	73	2.5
2	12	23	40	65	76	1.5
3	52	24	41	64	77	0.5
bulk	2000	23	41	84	69	

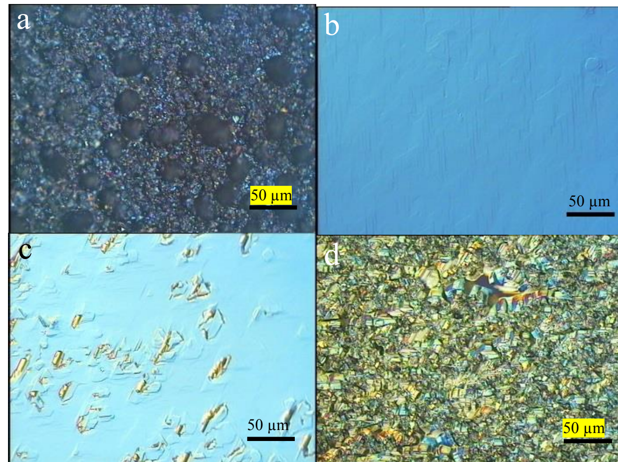


Figure 1. NDIC images of 3C epilayers grown at (a) 1325 °C (b) 1350 °C (c) 1375°C (d) 1400 °C with a fixed C/Si= 1, Si/H2 = 0.02%, C/N = 0.32% and the same C-rich ramp-up conditions. The thickness is approximately 20 μm for all the epilayers except 12 μm for the one in (c).

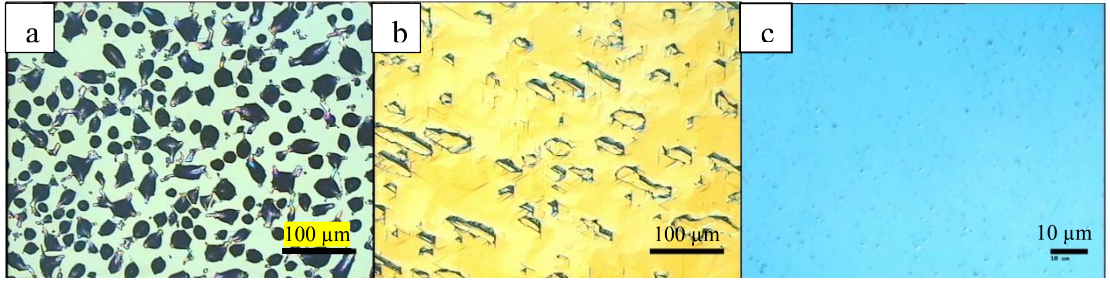


Figure 2. Optical microscopy images of 3C-SiC epilayers grown at 1350 °C with the same C-rich ramp-up condition, but at different C/Si ratios (a) 0.9 (b) 1.1. The thickness of these layers is about 19 µm. The Si/H2 ratio is (a) 0.022% and (b) 0.019%, respectively. (c) shows the surface morphology of a layer similar as in (a) but after wet chemical etching in HNO3:HF:CH3COOH= 5:3:3

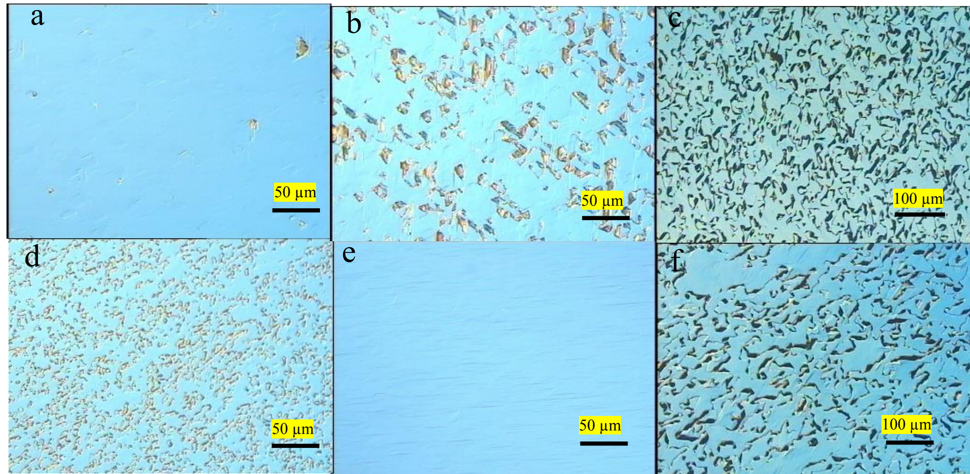


Figure 3. NDIC images of 3C-SiC epilayers with different ramp-up conditions. Different C3H8 flow rates of (a) 0.015% (b) 0.043% (c) 0.1% in H2 are used from room temperature to growth temperature. For (d)-(f), the ramp-up is performed under H2 and once the growth temperature is reached, a 0.015% C3H8 in H2 treatment is conducted prior to the growth with varying times: (d) 0 min (e) 5 min (f) 15 min. All these ramp-up conditions are followed by the same growth step, experiments were done at 200 mbar, 1350 °C, C/Si = 1, Si/H2 = 0.015%. Only the growth time could vary, between 1 h and 4 h, giving a film thickness comprised between 4 µm to 16 µm. The growth rate is constant of 4 µm/hr.

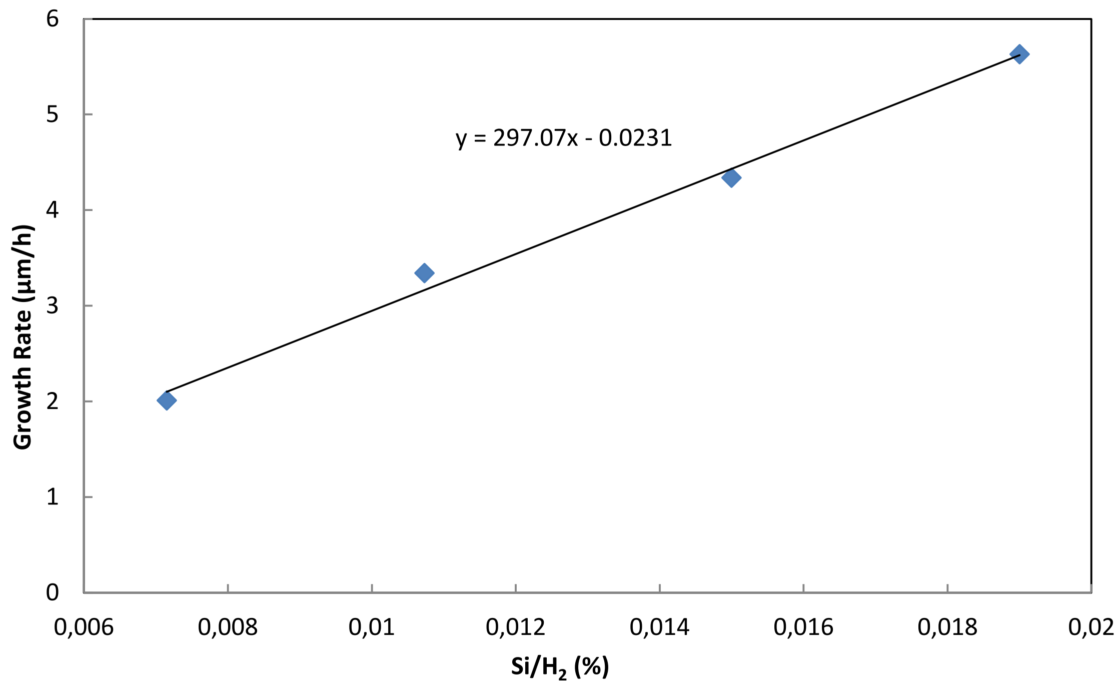


Figure 4. Growth rates for various silicon molar fractions. The growth runs were done at 1350 °C, 200 mbar, C/Si = 1, C/N = 0.32%. The insert line is the linear trend of these points.

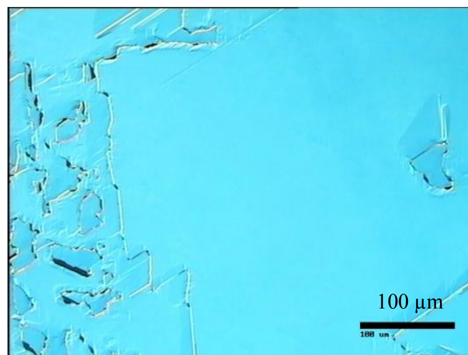


Figure 5. 3C-SiC on 6H-SiC substrate performed at 1350 °C, 200 mbar, C/Si = 1, Si/H2 = 0.015% and C-rich ramp-up condition.

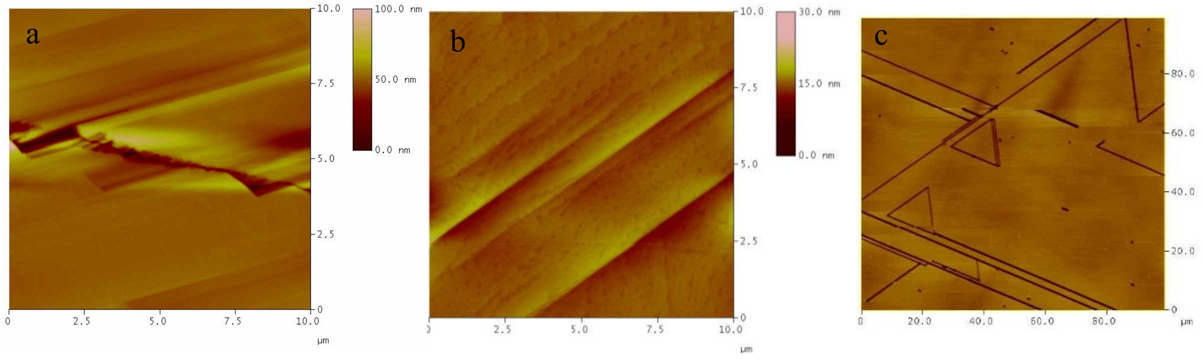


Figure 6. 10x10 µm2 AFM top view images of (a) a boundary between two domains of a 20 µm thick 3C sample with DPBs, (b) the same sample as in Fig. 3e and (c) 100x100 µm2 AFM top images of a single domain sample after KOH etching.

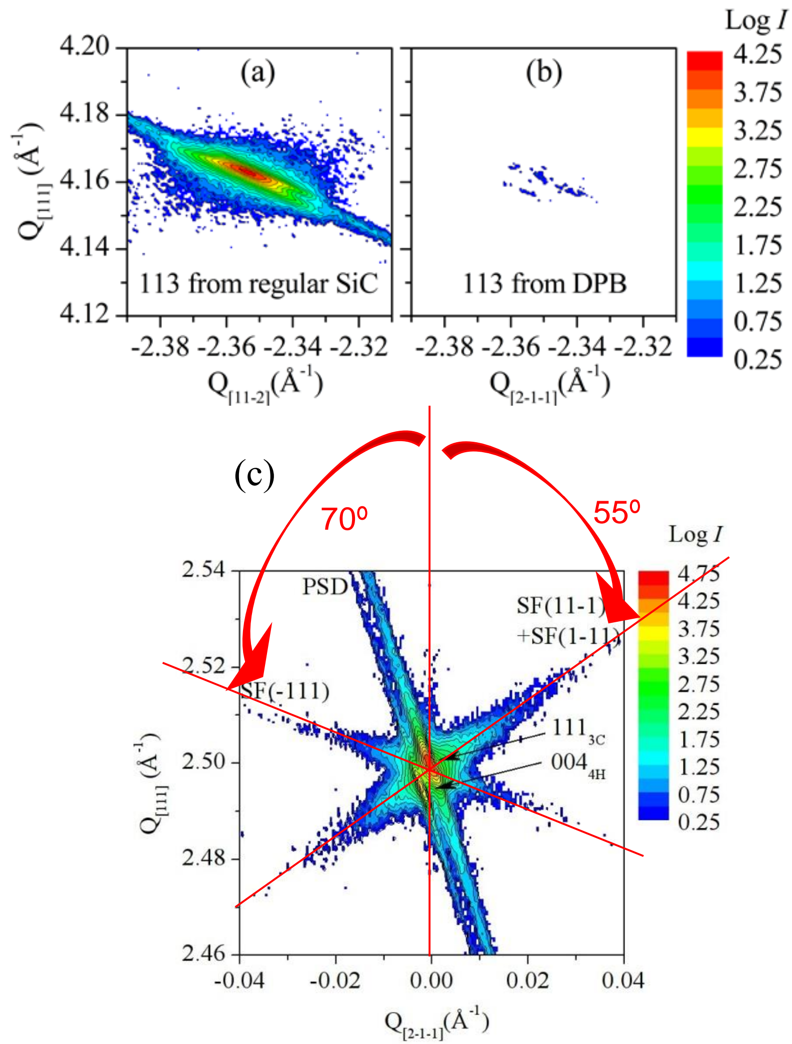
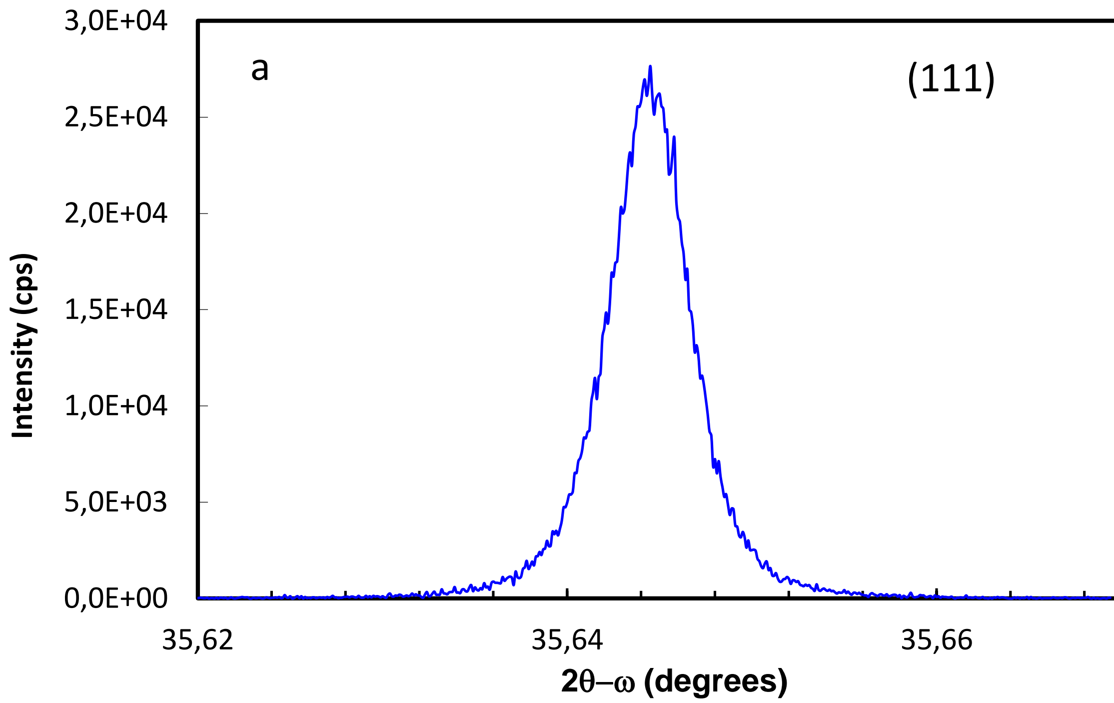


Figure 7. Reciprocal space maps for a 12.5 μm thick epilayer of the (a) (113) diffraction peak for maximum intensity, (b) (113) diffraction peak after 60º rotation around the crystal symmetry axis and (c) (111) diffraction peak.



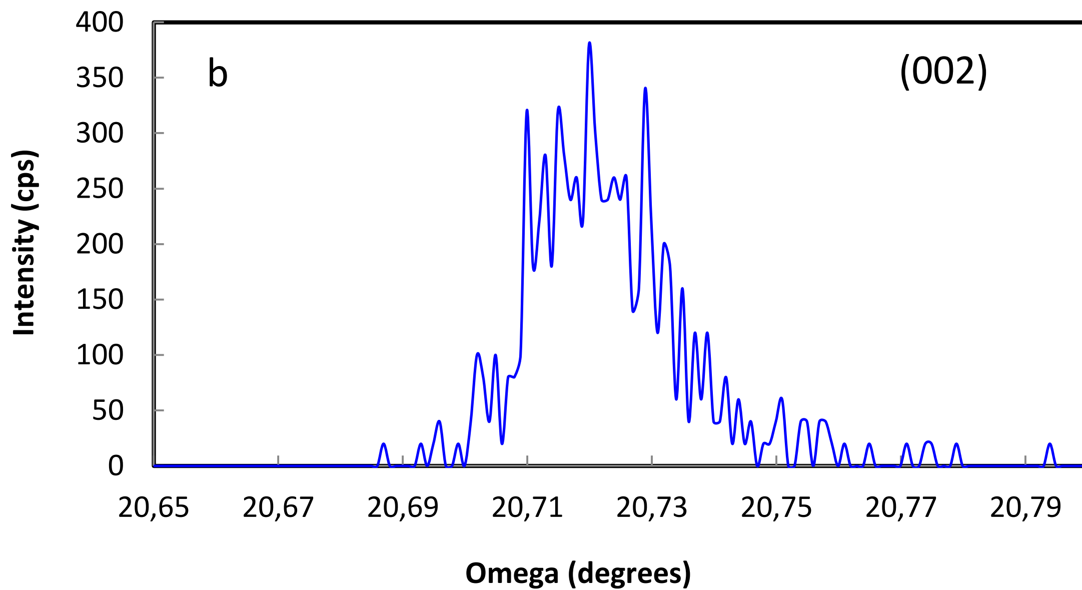


Figure 8. (a) 2θ-ω HRXRD spectrum of (111) reflection and (b) rocking curve of (002) reflection for a 35 μm thick 3C on 4H-SiC epilayer.

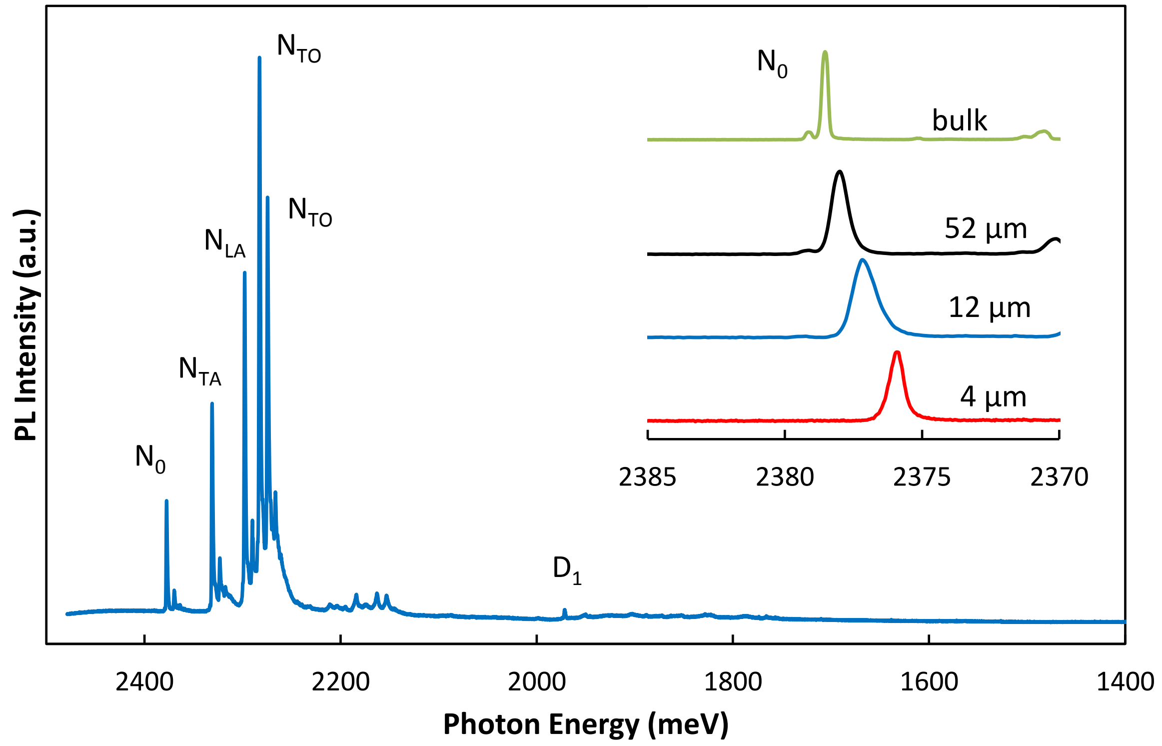


Figure 9. LTPL spectrum at 2K of the same sample as in Fig. 3e. The inset shows the near-band gap emission for three different layers with the indicated thickness together with the recorded spectrum from a bulk 3C sample.