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CVD growth and properties of on-axis vanadium doped semi-insulating 4H-SiC epilayers

Robin Karhu¹⁾, Einar Ö. Sveinbjörnsson^{1, 2)}, Björn Magnusson³⁾, Ivan G. Ivanov¹⁾, Örjan Danielsson¹⁾, Jawad Ul Hassan¹⁾

¹⁾Department of Physics, Chemistry and Biology (IFM), Linköping University, SE-581 83 Linköping, Sweden

²⁾Science Institute, University of Iceland, IS-107, Reykjavik, Iceland

³⁾Norstel AB, Ramshällsvägen 15 SE-602 38 Norrköping, Sweden

Abstract

Highly resistive homoepitaxial layers of 4H-SiC have been grown on the Si-face of nominally on-axis, n-type substrates using chemical vapor deposition (CVD). Vanadium tetrachloride has been used as V-dopant which is responsible for the high resistivity of the epilayers. 100% 4H-polytype was reproduced in the epilayers using optimized on-axis growth process and the upper limit of Vanadium tetrachloride flow rate for achieving defect-free high resistivity homoepitaxial layers was established. A resistivity of more than $1 \times 10^5 \Omega\text{-cm}$ has been achieved in epilayers with a very low concentration of V ($1 \times 10^{15} \text{ cm}^{-3}$). Owing to the low concentration of V, superior epilayer structural quality was achieved compared to V-doped and standard high purity semi-insulating bulk grown material of similar resistivity. Epitaxial layers with varying Vanadium tetrachloride flow have also been grown to study the influence of V concentration on the polytype stability, structural quality and optical and electrical properties of epilayers. A clear correspondence has been observed in the flow-rates of Vanadium tetrachloride, the atomic concentration of V and electrical, optical and structural properties of epilayers.

1. Introduction

Silicon Carbide (SiC) is a wide bandgap semiconductor of interest for high power and high-frequency electronic applications due to its high thermal conductivity, high breakdown electric field, and high saturation electron drift velocity. Among several polytypes of industrial importance, more specifically cubic 3C-SiC, and the hexagonal 6H- and 4H-SiC polytypes, the latter has been widely explored in terms of growth and characterization and thus has the highest maturity. The growth of 4H-SiC is well-developed nowadays and both bulk wafers and epitaxial layers are commercially available.

Semi-insulating (SI) 4H-SiC has been of particular interest for high-frequency device fabrication, such as SiC-based high-power micro-wave devices and GaN-based high electron mobility transistor (HEMT) devices¹, where SI 4H-SiC is used as a substrate material. SI substrates are required in high-frequency devices to minimize the parasitic capacitance.

Several methods for achieving SI 4H-SiC bulk substrates have been successfully demonstrated in the past. The different methods used to obtain SI material can be divided into two groups depending on whether the method uses intrinsic or extrinsic defects for the compensation of shallow dopants. Bulk SI substrates produced using intrinsic defects are commonly called high purity semi-insulating (HPSI) substrates. In this case, a common approach is to perform growth (e.g., sublimation growth) at very high temperatures to intentionally introduce high concentrations of intrinsic defects, such as C-vacancies (V_c) which compensate donors². Another method uses the high-temperature chemical vapor deposition (HTCVD) technique combined with ultra-high purity source gasses to achieve high resistivity material³. HPSI substrates produced using intrinsic defects or high purity growth process are difficult to grow and are more expensive than standard n-type substrates.

In the group which uses extrinsic defects, Fe and V have been the most researched dopants that can produce SI properties^{4, 5}, but V was studied more extensively. V substitutes silicon in the 4H-SiC lattice and acts as an amphoteric defect; the position of the Fermi level determines whether the defect acts as a donor or as an acceptor. This substitutional defect possesses three charge states in 4H-SiC, V^{4+} (neutral), V^{3+} (negatively charged), and V^{5+} (positively charged). Therefore, there exist two charge transition (deep) levels in 4H-SiC, $V^{4+/3+}$, and $V^{4+/5+}$, which act as acceptor and donor, respectively. The acceptor level is located at $E_C-0.97$ eV^{2, 6} and the donor level at $E_C-1.57$ eV⁷.

Highly resistive bulk substrates have been produced using V-doping⁵. However, a high concentration of $V > 1 \times 10^{17} \text{ cm}^{-3}$ is required to compensate the unintentional high background nitrogen doping concentration which is hard to control during sublimation bulk growth. However, high V concentration is shown to deteriorate the crystalline quality and has a negative influence on the device performance⁸⁻¹⁰. On the other hand, CVD growth has the natural advantage of better control over unintentional background doping due to high purity of gasses, lower growth temperature, and the possibility to tune the C/Si ratio during growth. A background n-type doping as low as $1 \times 10^{14} \text{ cm}^{-3}$ can be easily achieved. A lower background doping level would also require lower V concentration to attain high resistivity in the material and, hence, much higher crystalline quality can be maintained. Thus, an alternative approach for obtaining SI substrates for various applications would be to use V-doped epitaxial layers grown on common and low-cost conducting substrates.

SI epilayers of 4H-SiC have already been reported using V as a dopant on off-axis substrates^{11, 12}. However, off-axis epilayers cannot be used as a substrate for the growth of GaN-based HEMT structure because the growth of GaN-based HEMT structure is developed only for the Si-face of on-axis (0001) substrates. Therefore, on-axis homoepitaxial growth of

4H-SiC doped with V needs to be developed in order to realize suitable substrates for GaN HEMT structures. This task is challenging due to the polytypism of SiC, as discussed below.

SiC has many different polytypes which can be viewed as different stacking sequences of the Si-C bilayers along the (111) direction of the simplest cubic 3C-SiC polytype with the zincblende structure. The 4H and 6H polytypes are the most common hexagonal polytypes with their crystal axis (c-axis) coinciding with the direction of bilayers stacking. Epitaxial layers are generally grown on off-cut substrates to reproduce the substrate's polytype into the epilayer, i.e., the c-axis is tilted under a certain angle with respect to the surface normal of the substrate. Epitaxial growth on on-axis substrates (c-axis coincides with the surface normal) is problematic just because of the polymorphism because during on-axis growth small 3C islands nucleate on wide terraces and continue to grow as large 3C-SiC domains in the epilayer. Nevertheless, despite the difficulties in controlling the polytype, on-axis growth has been demonstrated on both C- and Si-face of 4H-SiC^{13, 14}. The main purpose of that work was to eliminate basal plane dislocations in the epilayer which in the case of off-axis growth replicate into the epilayer from the substrate and cause bipolar degradation in SiC-based bipolar devices during forward voltage injection.

In the present study, a method for growing low-cost on-axis V-doped high resistivity 4H-SiC homoepitaxial layers on n-type substrates was developed. High structural quality and high resistivity epilayers were grown by this method and may have applications in micro- and radiowave applications based on SiC and III-nitrides homo- and heteroepitaxial device structures.

2. Experimental

Nominally on-axis, Si-face polished, n-type, 100 mm diameter 4H-SiC (0001) wafers with unintentional off-cut within the range of 0.01-0.05° were cut into 16x16 mm pieces to be used

as substrates. Epitaxial growth was performed using a horizontal hot-wall CVD reactor with propane (C_3H_8) and silane (SiH_4) as precursors highly diluted in hydrogen. V-doping was achieved by introducing vanadium tetrachloride (VTC; VCl_4) during growth. The growth pressure and temperature were kept constant at 100 mbar and 1700 °C, respectively. In-situ surface preparation of the substrates prior to growth was performed in hydrogen at 1700 °C for 5-10 min. The growth process was optimized to achieve 100% 4H-polytype in the epilayer at a growth rate of 6-7 $\mu m/h$ without any intentional doping and the nitrogen background doping was brought down to the low 10^{14} cm^{-3} range. After establishing conditions for the on-axis homoepitaxial growth process, V was introduced during growth and the flow of VTC was adjusted to eliminate V related 3C-SiC domains and defects. A set of samples (V_1 - V_5) with different flow rates of VTC were also grown with all other growth parameters fixed, in order to study the efficiency of V incorporation in the epilayer with respect to the VTC flow rate, as well as the influence of V concentration on structural, optical and electrical properties of epilayers. The flow rates of VTC for these wafers were varied in the range of 0.01-0.001 sccm and the epilayers were grown to a thickness of 25 μm . The surface morphology was studied by optical microscopy with Nomarski differential interference contrast. The crystal quality of the epilayers was investigated using X-ray diffraction (XRD) ω -rocking curves. Optical and electrical properties of epilayers were studied using low-temperature photoluminescence (LTPL) spectroscopy, current-voltage (IV) and capacitance-voltage (CV) characterization. For the CV and IV measurements, 1.2 mm diameter Ni-contacts were evaporated on the epilayers and Ag-paste was applied to the back of the substrates. The IV measurements were performed at temperatures ranging from 25-200 °C. LTPL measurements made in the near-band-edge region at a temperature of 2 K and an excitation source with 351 nm wavelength, were used to study the behavior of nitrogen bound and free excitons in the epilayers. The LTPL spectrums made in the infrared region at a temperature of 3.5 K and an excitation

source of 514.5 nm wavelength has been used study luminescence from V. LTPL mapping was used to confirm the 4H-polytype and absence of other polytype inclusions in the epilayers. The atomic concentration of V in the epilayers was estimated using secondary ion mass spectrometry (SIMS). The SIMS data has been used to correlate the flow rate of VTC with V concentration in grown epilayers.

3. Results and discussion

3.1. On-axis homoepitaxial growth on the Si-face of 4H-SiC (0001)

As mentioned above, avoiding simultaneous nucleation of 3C-SiC during 4H-SiC homoepitaxy on the Si-face of on-axis substrates has been a major challenge. Lack of high-density steps on the surface of on-axis substrates leads to spontaneous nucleation of 3C-SiC domains, as shown in the optical image of a 12 μm thick epilayer grown on the Si-face of on-axis 4H-SiC substrate, shown in Fig. 1a. This image was taken with an automatic mapping system where small images are stitched together to generate an optical image of the whole sample. The surface of the whole sample was covered with irregular features which can be seen more clearly in Fig. 1b which is a high magnification image taken from the central region of the same sample shown in Fig. 1a. The irregularly shaped features are 3C-SiC domains and can be easily identified with optical microscopy due to the extremely smooth surface whereas 4H-SiC regions are covered with large steps and hillocks. 3C-SiC domains can be considered as large area defects in 4H-SiC epilayers.

The steps on the surface of the substrate can be formed through preferential etching around threading screw dislocation (TSD) intersecting the surface by high-temperature in-situ etching in hydrogen. Under optimized conditions, the surface step structure can be maintained during

Figure 1: Optical image taken from 16x16 mm samples with 12 μm thick epilayer grown with (a) standard epitaxial growth process and (b) is a high-magnification image taken from the central region of the same sample, the 3C-SiC domains and 4H-SiC regions are marked. (c) Illustration of the optimized on-axis growth process, no 3C-SiC domains are visible and (d) is a high magnification image, taken from the central region of the same sample showing typical 4H-SiC related spiral and step like features on the surface.

growth and 4H-SiC can be reproduced in the epilayer through growth on TSDs related steps, as shown in the optical image taken from a 12 μm thick homoepitaxial layer grown on a substrate taken from the same wafer, given in Fig. 1c. No 3C-domain-like features are found in this sample which is further confirmed by the high magnification image given in Fig. 1d, from the central region of the sample. 4H-SiC appears with unique characteristics of large

steps and/or hillocks and can be easily distinguished from the 3C-SiC domains. The uniform coverage with the 4H-SiC polytype in this epilayer was also confirmed by LTPL mapping of the sample using the near-band-edge (NBE) emission at 2K and no 3C-polytype related emission was observed on the low-energy side of the spectra. As can be seen in Fig. 1d, the surface morphology of the on-axis epilayer is inhomogeneous and significantly rougher compared to that of the epilayers grown on standard 4° off-axis substrates. This is mainly due to the lack of control over the growth mechanism on the on-axis surface. The growth is driven by spiral growth around threading screw dislocations whereas step-flow growth is dominant in regions where local off-cut due to basal plane bending is larger than 0.1°¹⁵.

The in-situ etching of the substrates prior to the growth was found to be crucial for obtaining 4H-SiC homoepitaxial layers without 3C-SiC domains. The in-situ etching temperature, ambient conditions and etching time are the most significant parameters to develop a suitable step structure on the surface of the substrate. During growth, the most significant parameters were determined to be the growth temperature, C/Si-ratio, and Si/H ratio to maintain the 4H-SiC polytype in the epilayer.

3.2. V-doped SI epilayers

3.2.1. Influence of V concentration on defects and polytype stability in the epilayer

Though an optimized on-axis growth process was used to achieve V-doped epilayers through an initial VTC flow rate of 0.05 sccm, the grown epilayers showed a high concentration of defects which otherwise were completely controlled under the same growth conditions but without VTC flow. This indicates that these defects are somehow related to VTC. A high concentration of V in the gas phase has been shown to produce a high density of defects in the epilayers grown on off-axis substrates^{12, 16}. The defects were mainly originating in the basal plane and grow larger with the increasing thickness of epilayer. Similar trends have been

Figure 2: Optical images of epilayers grown with different VTC flows, a) 0.05 sccm, V-related defects and 3C-SiC domains are indicated with arrows, b) 0.02 sccm, 3C-SiC domains are indicated with arrows and c) 0.01 sccm, the layer is completely free of V-related defects and 3C-SiC domains.

observed in V-doped on-axis homoepitaxial layers, but the nature of defects is different from that of off-cut substrates. On-axis layers mainly showed a high concentration of 3C-SiC domains and V-related defects that are presumed to be related to V-precipitates (Fig. 2a). V-precipitate like defect is similar to the defects reported for bulk crystals grown with a high concentration of V¹⁷. In bulk grown crystals, such defects are believed to be formed due to the low solubility of V in SiC^{8, 17}. A significantly lower growth temperature used for epitaxial growth, compared to the bulk growth process, lowers further the solubility limit of V in SiC and V-precipitate like defects can be easily formed. The formation of 3C-SiC domains indicates that VTC also disturbs the polytype stability in the epilayer. 3C-SiC domains were mainly formed on top of V-related defects, as seen in the optical image shown in Fig. 2a, indicating that these defects are probably triggering the formation of 3C-SiC domains.

To eliminate V-related defects and 3C-SiC domains, the VTC flow rate was gradually decreased during a series of growth runs. The growth runs were made under the same growth conditions while the VTC flow rate was lowered from 0.05 to 0.01 sccm. A gradual reduction and ultimately complete elimination of V-related defects and 3C-SiC domains were observed with decreasing flow rate of VTC, as shown in the optical images in Fig. 2a-c, taken from

three different samples grown with VTC flow rates of 0.05, 0.02 and 0.01 sccm, respectively. V-related defects already vanished or at least are not visible at a reduced flow rate of VTC at 0.02 sccm, as shown in Fig. 2b, however, 3C-SiC domains were still present. It is assumed that the V-related defects are still present in this sample, but on a scale, which makes them invisible under an optical microscope. We believe that such defects, even when they are on the microscopic scale, still source the nucleation of 3C-SiC domains, as illustrated in Fig. 2b. This indicates that the formation of 3C-SiC is extremely sensitive to the flow rate of VTC. A further reduction in the flow rate of VTC to 0.01 sccm completely eliminates the 3C-SiC domains, as shown in the optical image in Fig. 2c. Based on the experimental results, this is probably the highest possible flow rate of VTC under the given growth condition to achieve defect-free on-axis epilayer without disturbing polytype stability. Hence this flow rate was set as the upper limit for the VTC flow rate.

We further investigated the incorporation of V in the epilayers depending on the flow rate of VTC during growth, as well as the influence of V concentration on the structural, optical and electrical properties of epilayers. A series of 25 μm thick samples V_1 to V_5 was grown. The samples were grown starting with the highest VTC flow rate for sample V_1 and decreasing the flow rate with increasing sample number. All the growth parameters were kept constant including the growth rate while the VTC flow rate was changing from 0.01 sccm for sample V_1 to zero for sample V_5 . Thus, the last sample V_5 grown without VTC flow allows us to study the memory effect of V in the susceptor. The flow rates of VTC for all samples are given in Table 1. A stable 4H-SiC polytype has been observed in all epilayers and no difference has been observed in the surface morphology of epilayers in the described series grown with different flow rates of VTC.

Sample name	VTC flow [sccm]	Atomic concentration of V [cm ⁻³]
V ₁	0.01	2x10 ¹⁶
V ₂	0.006	-
V ₃	0.004	7x10 ¹⁵
V ₄	0.001	-
V ₅	0	1x10 ¹⁵

Table 1: Sample name and corresponding VTC flow used during growth. The third column contains V concentration as measured by SIMS for a subset of the samples.

3.2.2. SIMS analysis

The SIMS measurements have been performed commercially at EAG Laboratories using O₂⁺ as primary ion beam (for V, B and Al). The atomic concentration of V in three selected samples, V₁, V₃ and V₅, determined by SIMS measurements was found to be about 2x10¹⁶, 7x10¹⁵ and 1x10¹⁵ cm⁻³, respectively, corresponding to the decreasing flow rates of VTC during growth, given in Table 1. This indicates that the incorporation of V during epitaxial growth can be controlled effectively by controlling the flow rates of VTC. The doping depth profile of residual B and Al was also measured through SIMS to be able to see the relative concentration in the epilayers doped with a low concentration of V. The SIMS detection limits for B and Al are 2x10¹³ and 3x10¹³ cm⁻³, respectively. The observed concentrations of residual B and Al impurities in all epilayers are well below the concentration of V, at a constant level and very close to the detection limit of SIMS. We noticed homogeneous V doping within the probed depth of the samples. A rather high concentration of V (1x10¹⁵ cm⁻³) in the undoped epilayer V₅ shows that V has a strong memory effect in the epilayer grown immediately after V-doped growth runs.

Sample V_5 was grown to determine the memory effect of V in the growth cell. For the rest of the study, this sample is used together with other samples in the series to investigate the influence of V concentration on the structural, electrical and optical properties of the epilayers.

Figure 3: SIMS data from samples V_1 , V_3 and V_5 grown using VTC-flow of 0.01, 0.004 and 0 sccm, respectively. A high concentration of V in V_5 sample indicates a strong memory effect immediately after V-doped growth runs.

3.2.3. Structural properties

V is a substitutional impurity replacing the Si atom in the SiC host lattice. It has been reported that a high V concentration leads to deteriorated crystalline quality of both bulk grown crystals and epitaxial layers^{4, 17}. This is mainly expressed in the formation of a high density of defects especially low angle grain boundaries, possibly due to the relatively large size of the V atom compared to Si. The ω -rocking curves of the reflection from the (0 0 0 4) planes of samples V_5 to V_1 displayed in Fig. 4 show a gradual increase in the full width half maximum (FWHM) with the increasing V concentration in the epilayers. Nevertheless, the crystalline

Figure 4: ω -rocking curves of (0 0 0 4) planes obtained from samples V₁ – V₅. which corresponds to VTC flow of 0.01, 0.006, 0.004, 0.001 and 0 sccm, respectively.

quality of the V₁ sample grown with the highest flow rate of V (0.01 sccm) is much better compared to the quality of the previously reported V-doped bulk crystals and epitaxial layers. The FWHM of the ω -rocking curve of V₁ sample is just 36.6 arcsec, which is significantly lower compared to the FWHM values of 100 arcsec reported for V-doped SiC bulk crystal with similar resistivity¹⁸. A significant decrease in the FWHM of the ω -rocking curve (22.8 arcsec) is observed for the V₂ sample. Further decrease in the FWHM of ω -rocking curves for the rest of the samples was observed with decreasing V concentration and for the V₄ sample, grown with a minimum flow rate of VTC (0.001 sccm), and the V₅ sample grown without any flow of VTC, it is about 18 arcsec. The shape of the ω -rocking curve becomes symmetric for VTC flow below ~ 0.004 sccm and the FWHM-values are very similar to those of standard n-type bulk 4H-SiC crystals which indicate that no additional V-related defects or low angle grain boundaries are formed during epitaxial growth. This is a strong evidence that V-doping can be used to achieve high resistivity on-axis epitaxial layers without any degradation of crystal quality.

3.2.4. Electrical properties

The electrical properties were investigated using IV and CV analysis. A schematic of the sample structure is shown in Fig. 5. The Ni contacts on the V-doped epilayer form Schottky

Figure 5: Schematic of the sample used for IV and CV analysis. diodes while the contact made on the wafer backside (highly N-doped) using Ag paste is ohmic. In order to obtain information on the resistivity of the V-doped epilayer, the Ni Schottky diodes were investigated using the wafer backside as the ohmic contact.

3.2.4.1. IV analysis

Figure 6 shows the IV curve of sample V_5 at room temperature. The sample shows rectifying behavior with the Schottky diode turning on between 1 and 2 V. Due to the high resistivity of the V-doped epilayer the current is limited by the series resistance above 2 V and increases approximately linearly with voltage. The series resistance is extracted from the slope of this linear part in the IV curve between 3 and 10 V, as shown in Fig. 6b. This gives an estimate of the resistivity of the V-doped layer which is approximately $2 \times 10^5 \Omega\text{-cm}$. V_4 shows a similar

Figure 6: a) Current vs. voltage measured at room temperature on the sample labeled V_5 . b) contains a linear fit between 3 and 10 V.

Figure 7: IV curve from sample V₂ taken at 200 °C.

IV behavior and the resistivity extracted at room temperature is about $4 \times 10^5 \Omega\text{-cm}$. IV curves of samples V₄ and V₅ were also recorded at 150 and 200 °C. The resistivity extracted at elevated temperatures did not change markedly for these two samples as compared to room temperature (V₄ and V₅ have a resistivity of $\sim 2 \times 10^5 \Omega\text{-cm}$ and $\sim 6 \times 10^5 \Omega\text{-cm}$, respectively).

IV analysis was also made on samples V₁-V₃. All these samples show no detectable current at room temperature (less than 10 pA). However, a rectifying behavior was observed at 150 and 200 °C in these samples. Figure 7 shows the IV curves for V₂ at 200 °C. The forward bias current is limited by the series resistance and the resistivity of the V-doped epilayer extracted from this data is $\sim 2 \times 10^8 \Omega\text{-cm}$. The value for V₂ at 150 °C is $\sim 3 \times 10^9 \Omega\text{-cm}$ which shows that the resistivity decreases with increasing temperature in agreement with previous findings in highly V-doped SiC¹⁷. Samples V₁ and V₃ show very similar results. The resistivity at 200 °C is within the range $2\text{-}4 \times 10^8 \Omega\text{-cm}$ and $3\text{-}5 \times 10^9 \Omega\text{-cm}$ at 150 °C for samples V₁-V₃.

3.2.4.2. CV analysis

The Schottky diodes of samples V₁-V₅ were also analyzed with CV at room temperature and at 150 °C. Samples V₁-V₃ all show constant capacitance of $\sim 5.5 \text{ pF}$ with no bias dependence (see Fig. 8a). This capacitance value agrees approximately with the expected depletion layer capacitance when the whole 25 μm thick V-doped epilayer is depleted. Assuming a built-in

Figure 8: CV measurements made at room temperature on samples a) V₁ and b) V₅.

potential of the Schottky diode of ~ 2 V we get an upper limit of the net carrier concentration in samples V₁-V₃ of $3.7 \times 10^{12} \text{ cm}^{-3}$.

The resistivity estimates from the IV analysis made in the previous section suggest that the net carrier concentration is most likely orders of magnitude lower than this upper limit obtained from CV. In contrast, it is possible to extract the net donor doping concentration in samples V₄ and V₅. Figure 8b shows the CV behavior of sample V₅ at room temperature. The CV shows a typical behavior of an n-type Schottky diode. A plot of $1/C^2$ vs. V shows a linear behavior which points towards a uniform net donor concentration within the epilayer. The net donor concentration extracted from this data is $1 \times 10^{14} \text{ cm}^{-3}$ and the same value within experimental error was extracted from CV data recorded at 150°C (not shown). This is significantly higher net doping concentration than expected from the IV data where the resistivity was estimated to be in the $10^5 \Omega\text{-cm}$ range which would suggest a net doping concentration in the 10^{12} cm^{-3} range, assuming a bulk electron mobility value as in low doped SiC around $700 \text{ cm}^2/\text{Vs}$. However, Hall mobility on the order of $10 \text{ cm}^2/\text{Vs}$ has been reported

in V compensated 4H-SiC¹⁹. It is therefore probable that the mobility is significantly lower in our heavily compensated material than the bulk mobility in low doped SiC which could explain most of this difference. Nevertheless, even with such an assumption, there is some discrepancy between the IV and CV data that cannot be explained at the present time.

The resistivity variations of V compensated 6H-SiC with respect to the net density of shallow dopant donor and acceptors have been carefully investigated by Bickermann *et. al.*¹⁷. The acceptor and donor levels of V in 6H-SiC are located at almost the same energies as in 4H-SiC (at $E_c-0.9$ eV and $E_c-1.7$ eV respectively) and the behavior is similar as in 4H-SiC¹⁹⁻²¹. The resistivity in 6H-SiC that is fully compensated with V and contains a higher density of shallow acceptors than donors, exhibits 3-4 orders of magnitude higher resistivity than material containing a higher density of shallow donors. This is related to Fermi-level pinning near the donor and acceptor levels of V¹⁷. In nominally p-type material, the fermi-level is pinned close to the V donor level at $E_c-1.6$ eV and there is insignificant residual carrier concentration in the sample. In nominally n-type material, the fermi-level is close to the V acceptor level at $E_c-0.9$ eV and there is a residual electron concentration in the conduction band due to thermal emission of electrons from the V acceptor level. This agrees very well with our IV and CV data. The samples are nominally n-type and the fermi-level is then located near the V acceptor level. When the V concentration increases (samples V₅ through V₁) the Fermi-level moves downwards and the residual electron concentration decreases. An increase in the measured resistivity and the decrease in net carrier concentration of epilayers V₅-V₁ is consistent with the increasing flow rate of VTC used during growth. It is in principle possible to increase the resistivity even further if the epilayers would be made nominally p-type due to the Fermi-level pinning near the V donor level which would result in a negligible net carrier density.

3.2.5. Optical properties

We have studied also the LTPL of the samples, both in the NBE region and in the infrared region where the PL lines associated with intrinsic V transitions are observed¹⁷. The results are displayed in Fig. 9. Let us consider first the spectra in the NBE region where the emission from shallow dopants (N in this case) and free excitons (FE) was observed (see Fig. 9(a)). The nitrogen-bound excitons (N-BE) are represented by two zero-phonon lines (denoted P_0 and Q_0), which correspond to the two donor sites, hexagonal and cubic, respectively, as well as the phonon replicas mainly of the P_0 line. The latter is denoted as P_x in Fig. 9(a), where the subscript 'x' is the approximate energy in meV of the phonon involved in the exciton recombination. Whenever visible, some of the prominent phonon replicas of the FE are denoted by I_x in the same manner (the zero-phonon line for FE is forbidden due to momentum conservation)²². Note that the broad-band emission from the substrate has nearly the same intensity in all samples because it is excited by the laser at 351 nm penetrating through the epilayers (about 40 μm penetration depth²³) and the thickness of all epilayers is nearly the same. One can see from Fig. 9(a) that the exciton-related emission (FE and N-BE) decreases with increasing V concentration and nearly vanishes in the sample V_1 with the highest V-doping. Thus, the excitons created in the epilayer by the above-band-gap excitation at 351 nm are consumed by another defect, and we have good evidence that this defect is V. Indeed, the intensity of infrared α - and β -lines due to intrinsic transitions in the V atom increase by at least three orders of magnitude in all samples if excited above the band gap with 351 nm (not shown), compared to the same lines excited with below band gap 514.5 nm laser shown in Fig. 9(b). This leads us to conclude that V is very efficient in capturing free excitons and its increasing concentration is the main reason for quenching the NBE luminescence.

On the other hand, below band gap excitation (514.5 nm in our case) also excites, albeit weakly, the V-related intrinsic transitions, as shown in Fig. 9(b). Interestingly, in this case, the intensity of the strongest α -line at 1278 nm in the spectra displayed in Fig. 9(b) scales

Fig. 9 LTPL spectra showing (a) the near band edge (NBE) luminescence of the $V_1 - V_5$ samples at 2K excited by a 351 nm laser. The VTC flow rate is denoted for each curve. Using common notations, the free-exciton phonon replicas are labeled I_x , whereas the nitrogen-bound-excitons are labeled P_x , where the subscript ‘x’ denotes the approximate energy of the involved phonon in meV. Q_0 and P_0 denote the zero-phonon lines of the nitrogen-bound excitons at cubic and hexagonal lattice sites, respectively. The broad background comprising five broad bands (indicated by arrows in the bottom curve near the top of each band) are due to the substrate. (b) Spectra from the $V_1 - V_4$ samples recorded in the IR region at 3.5 K using 514.5-nm laser excitation. The α - and β -lines associated with V intrinsic transitions are seen²⁴.

approximately with the VTC flow (and, presumably, with the V concentration) for the different samples. Indeed, the intensities of this line are related as 1:0.95:0.42:0.06 for $V_1: V_2: V_3: V_4$, respectively, whereas the corresponding VTC-flow ratios are 1:0.6:0.4:0.1. In

addition, the concentration ratio of the $V_1:V_3$ samples measured by SIMS, 1:0.35, is also in very good agreement with the intensity ratio of the corresponding α -lines, 1:0.42, as quoted above. We notice that since the epilayer is essentially transparent for the 514.5 nm excitation, the observed intensities will be proportional not only to the V concentration but also to the thickness of the layers, which is assumed to be about the same for all layers ($\sim 25 \mu\text{m}$). In contrast to the below-gap excitation, when the infrared α - and β -lines are excited with above band gap excitation (351 nm, not shown), the intensity of the α - and β -lines increases enormously, as mentioned before, but the observed intensities are approximately the same (within a factor of ~ 2) for all samples and do not correlate with the V-doping concentration.

In Fig. 9 (a) the peak intensities of the FE and N-BE are significantly higher in samples V_4 and V_5 compared to the other samples. This, together with the significantly lower intensities of the α - and β -lines of sample V_4 compared to the other samples in Fig. 9 (b), correlates well with the much lower resistivity in these two samples measured by CV and IV.

Even though the sample V_4 was intentionally doped with a small flow of V whereas V_5 was grown without intentional doping. No difference has been observed in these samples regarding electrical, optical and structural properties, indicating that V concentration is probably similar in both samples and V has a strong memory effect. It has been suggested that, in order to avoid the penetration of bipolar plasma into the substrate and hence the formation of stacking faults in SiC-based PiN devices, V doping can be used in the buffer layer to effectively kill bipolar plasma²⁵. V has also shown to effectively control charge carrier lifetime in 4H-SiC epilayers, when used at very low and controlled concentration ($<1 \times 10^{13} \text{ cm}^{-3}$)²⁶. A strong memory effect indicates that strong baking of the reactor is required to bring background V concentration down and it would not be possible to continue the growth of pure thick intrinsic layer after the growth of highly doped V buffer layer.

4. Conclusions

On-axis homoepitaxy was employed to achieve V-doped high resistivity epilayers on n-type 4H-SiC substrates using VTC as V-source. A high flow rate of VTC resulted in the formation of V precipitate-like defects and disturbed the polytype stability in the epilayer through the formation of 3C-SiC domains. Under the optimized flow rate of VTC, it was possible to eliminate the V precipitate-like defects and 3C-SiC domains while still obtaining epilayers with high resistivity. The incorporation of V in epilayers depending on the flow rate of VTC during growth is confirmed by SIMS and LTPL. In particular, the intensity of the LTPL spectra in the infrared regions shows quantitative correlation with the available SIMS results and corroborates the notion that the V incorporation in the layers increases approximately proportionally to the VTC flow rate. However, the maximum possible flow rate of VTC to achieve epilayers free of V-precipitate like defects and 3C-SiC domains is limited to 0.01 sccm resulting in a V concentration of $\sim 2 \times 10^{16} \text{ cm}^{-3}$. This concentration is sufficient for compensating residual donor/acceptor impurities with a concentration below 10^{15} cm^{-3} in epitaxial layers, which provides a way for growing high-quality semi-insulating on-axis epilayers. The FWHM of the ω -rocking curves of the samples grown with different flow rates of VTC shows a clear dependence on the V-concentration, increasing from 18 to 37 arcsec with the increasing concentration of V from 1×10^{15} - $2 \times 10^{16} \text{ cm}^{-3}$. The resistivity of the sample with the lowest V concentration ($1 \times 10^{15} \text{ cm}^{-3}$) was above $1 \times 10^5 \Omega\text{-cm}$ at room temperature. The resistivity of samples with higher V concentration (between 6×10^{15} - $2 \times 10^{16} \text{ cm}^{-3}$) was too large ($>10^9 \Omega\text{-cm}$) to be estimated at room temperature but was in the $10^9 \Omega\text{-cm}$ range at 150 °C. The structural quality of the epilayer with the highest concentration of V was much better than that of the bulk grown V-doped and HPSI crystals. A high resistivity achieved with such a low concentration of V in epilayers is due to extremely low residual n-type doping (low 10^{14}

cm⁻³ rang). Such high resistivity and high-quality on-axis epilayers can be very useful in high-power microwave applications based on SiC and III-Nitrides technologies.

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6. References

1. S. T. Sheppard, K. Doverspike, W. L. Pribble, S. T. Allen, J. W. Palmour, L. T. Kehias and T. J. Jenkins, IEEE Electron Device Letters **20** (4) (1999).
2. T. Dalibor, G. Pensl, H. Matsunami, T. Kimoto, W. J. Choyke, A. Schöner and N. Nordell, phys. stat. sol. **162** (1997).
3. A. Ellison, B. Magnusson, C. Hemmingsson, W. Magnusson, T. Iakimov, L. Storasta, A. Henry, N. Henelius and E. Janzén, MRS Proceedings **640** (2001).
4. H. K. Song, S. Y. Kwon, H. S. Seo, J. H. Moon, J. H. Yim, J. H. Lee, H. J. Kim and J. K. Jeong, Appl Phys Lett **89** (15), 152112 (2006).
5. H. M. Hobgood, R. C. Glass, G. Augustine, R. H. Hopkins, J. Jenny, M. Skowronski, W. C. Mitchel and M. Roth, Appl Phys Lett **66** (11), 1364-1366 (1995).
6. N. Achtziger and W. Witthuhn, Phys Rev B **57** (19) (1998).
7. W. C. Mitchel, W. D. Mitchell, G. Landis, H. E. Smith, W. Lee and M. E. Zvanut, J Appl Phys **101** (1), 013707 (2007).
8. A. P. Zhang, L. B. Rowland, E. B. Kaminsky, J. B. Tucker, R. A. Beaupre, J. W. Kretchmer, J. L. Garrett, A. Vertiatchikh, G. Koley, H. Y. Cha, A. F. Allen, J. Cook, J. Foppes and B. J. Edward, Journal of Electronic Materials **32** (5), 437-443 (2003).
9. S. G. Muller, M. F. Brady, W. H. Brixius, R. C. Glass, H. M. Hobgood, J. R. Jenny, R. T. Leonard, D. P. Malta, A. R. Powell, V. F. Tsvetkov, S. T. Allen, J. W. Palmour and C. H. Carter, Silicon Carbide and Related Materials - 2002 **433-4**, 39-44 (2002).
10. A. V. Los, J Appl Phys **100** (1) (2006).
11. Y. Koshka, M. Mazzola, S. Yingquan and J. Pittman, C. U., Journal of Electronic Materials **30** (3), 220-223 (2001).
12. B. Krishnan, S. Kotamraju, R. V. K. G. Thirumalai and Y. Koshka, J Cryst Growth **321** (1), 8-14 (2011).
13. K. Kojima, H. Okumura, S. Kuroda and K. Arai, J Cryst Growth **269** (2-4), 367-376 (2004).

14. J. Hassan, J. P. Bergman, A. Henry and E. Janzén, *J Cryst Growth* (310), 4424-4429 (2008).
15. J. Ul Hassan, I. Booker, L. Lilja, A. Hallen, M. Fagerlind, P. Bergman, E. Janzen, A. Lebedev, S. Davydov, P. Ivanov and M. Levinshtein, *Silicon Carbide and Related Materials 2012* **740-742**, 173-176 (2013).
16. H. K. Song, S. Y. Kwon, J. H. Moon, H. S. Seo, J. H. Yim, J. H. Lee and H. J. Kim, *J Electrochem Soc* **155** (1), H11-H16 (2008).
17. M. Bickermann, R. Weingartner and A. Winnacker, *J Cryst Growth* **254** (3-4), 390-399 (2003).
18. A. K. Gupta, I. Zwieback, A. E. Souzis, M. Yoganathan and T. Anderson, *Materials Science Forum* **600-603**, 35-38 (2008).
19. W. C. Mitchel, R. Perrin, J. Goldstein, A. Saxler, M. Roth, S. R. Smith, J. S. Solomon and A. O. Ewaraye, *J Appl Phys* **86** (9), 5040-5044 (1999).
20. J. R. Jenny, J. Skowronski, W. C. Mitchel, H. M. Hobgood, R. C. Glass, G. Augustine and R. H. Hopkins, *Appl Phys Lett* **68** (14), 1963-1965 (1996).
21. M. E. Zvanut, V. V. Konovalov, H. Y. Wang, W. C. Mitchel, W. D. Mitchell and G. Landis, *J Appl Phys* **96** (10), 5484-5489 (2004).
22. I. G. Ivanov, U. Lindefelt, A. Henry, O. Kordina, C. Hallin, M. Aroyo, T. Egilsson and E. Janzén, *Phys Rev B* **58** (20), 13634-13647 (1998).
23. S. G. Sridhara, T. J. Eperjesi, R. P. Devaty and W. J. Choyke, *Materials Science and Engineering: B* **61-62**, 229-233 (1999).
24. J. Schneider, H. D. Müller, K. Maier, W. Wilkening, F. Fuchs, A. Dörnen, S. Leibenzeder and R. Stein, *Appl Phys Lett* **56** (12), 1184-1186 (1990).
25. T. Tawara, T. Miyazawa, M. Ryo, M. Miyazato, T. Fujimoto, K. Takenaka, S. Matsunaga, M. Miyajima, A. Otsuki, Y. Yonezawa, T. Kato, H. Okumura, T. Kimoto and H. Tsuchida, *Journal of Applied Physics* **120** (11) (2016).
26. T. Miyazawa, T. Tawara, R. Takanashi and H. Tsuchida, *Applied Physics Express* **9** (11) (2016).