Intentional Incorporation and Tailoring of Point Defects during Sublimation Growth of Cubic Silicon Carbide by Variation of Process Parameters

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Cubic silicon carbide (3C-SiC) is an emerging material with promising properties for various applications in power electronics, energy saving, and quantum technology. In recent years, size and quality of 3C-SiC substrates reached a level where real applications become tangible. However, there is still a lack of knowledge concerning defects in 3C-SiC. Point defects can be considered as one of the key defects, as they influence all applications in one way or another. Herein, the growth rate dependent tailoring of point defects—according to probability and density—is presented for bulk 3C-SiC grown by epitaxial sublimation growth. Photoluminescence characterization reveals a group of four distinct peaks in the near-infrared which are assumed to have their joint origin in the carbon vacancy. Moreover, indications for a novel Al-related defect are presented. The observed defects show bright luminescence in the 175 K/200 K regime and remain excitable up to 300 K.

1. Introduction

Silicon carbide (SiC) has by now firmly established as promising material especially for power electronics.[1–3] This is due to its outstanding physical properties, such as a wide bandgap, a high break-down field strength, high saturation drift velocity, high thermal conductivity, as well as radiation hardness and chemical resistance.[4] In recent years, the cubic polytype of silicon carbide (3C-SiC) has generated attention as it offers some advantages over its well established hexagonal counterparts. Due to the smaller bandgap of 2.3 eV, the near-interface-traps (NITs) of the 3C-SiC/SiO₂ system are located within the conduction bandgap of 2.3 eV, the near-interface-traps (NITs) of the cubic system are located within the conduction band.[5–8] In combination with reasonable high charge carrier mobilities, this enables the highest channel mobility among all SiC polytypes and therefore significant advantages for 3C-SiC-based metal-oxide-semiconductor field-effect transistors (MOSFETs). Considering doping of 3C-SiC with boron (B) and aluminum (Al), p-type material will not only offer new opportunities in power electronics but also for energy savings. Boron-doped 3C-SiC may act as an ideal material for intermediate band solar cells due to an almost perfect deep B-level within the bandgap.[9] Aluminum-doped 3C-SiC could lead to the development of efficient photoelectrochemical water-splitting cells for hydrogen generation.[10,11] Since Koehl et al.[12] published their remarkable work about defects in 4H-SiC which could act as spin qubits up to room temperature, SiC also attracted great attention in this field.[13–24] 3C-SiC could be advantageous in this area, too. In hexagonal SiC, the stacking of the Si-C bilayers gives rise to symmetry-invariant lattice sites of cubic or hexagonal character which results in a variety of electronic sublevels lying close together. The higher symmetry of the cubic crystal lattice eliminates the problem of symmetry-inequivalent configurations and leads to a more unique defect signature.[20] This allows the individual addressability of defects which is the prerequisite for the application of, e.g., integrated quantum optics.

Such applications require mature material with high structural quality and well-defined properties. Since Nishino et al.[25] published the pioneering work about a multi-step chemical vapor deposition (CVD) growth process in the early 1980s, serious efforts have been made to improve the material. Nowadays, 3C-SiC can be heteroepitaxially grown on silicon (Si) substrates with diameters up to 6 in. by CVD.[26] However, the mismatch of lattice parameters and thermal expansion coefficients between SiC and Si is technologically still not solved. This leads to high numbers of defects, especially stacking faults (SFs), and considerable stress resulting in a bow of the whole wafer. Substantial progress in thickness and quality of the available material has been made by applying epitaxial sublimation growth.[27,28]

However, irrespective of the aforementioned application, 3C-SiC is at the very beginning when it comes to the understanding of the generation, structure, and properties of defects, especially point defects within the material. All applications are in one way or another, positively or negatively, influenced by point defects. Therefore, deep knowledge of these defects can be considered as essential for further development of the material and applications based on 3C-SiC.
In this work, the in situ generation and tailoring of intentional point defects in bulk 3C-SiC during sublimation growth is studied. Furthermore, it is demonstrated that in situ doping can be used for defect engineering and the creation of defect complexes from intrinsic and extrinsic defects. Photoluminescence (PL) characterization revealed a group of at least four peaks in the near-infrared (NIR) which can be modified by growth rate or dopant concentration. The joint origin of the peaks is assumed to be the carbon vacancy.

2. Experimental Section

2.1. Epitaxial Sublimation Growth

Nitrogen- (N), boron- (B), and aluminum (Al)-doped freestanding, single crystalline 3C-SiC layers were prepared by epitaxial sublimation growth in our lab. Details of the growth setup were given in previous studies. For the characterizations in this work, samples of 12 × 12 mm² or pieces from 1 in. layers were used. The characterization was performed on as-grown surfaces with negligible native surface oxide. Dopant type and concentration were varied by the choice of the source material and determined by secondary-ion mass spectrometry (SIMS) or by estimation, assuming similar dopant concentration of sample and source material. It should be noted that even though doping was varied from n-type to p-type by selecting N-, B-, and Al-doped source wafers of different dopant concentrations, all samples (S) are unintentionally co-doped to a certain extent due to contaminations of the source material with N, B, and Al. Thickness and growth rate of the (100) and (111) oriented samples varied between 275 to 765 μm and 123 to 306 μm h⁻¹, respectively.

2.2. PL Characterization

Temperature-dependent PL measurements were performed between 26 and 300 K with a step size of 25 K using a CTI-Cryogenics closed-cycle He-cryostat in combination with a temperature controller LakeShore 330. A laser diode with 405 nm (Coherent CUBE 405-100C) in combination with a 405 nm bandpass as well as a 450 nm long pass filter was used for above bandgap excitation. All measurements were conducted with 50 mW laser power and a spot size of 900 μm in diameter. The penetration depths of the laser were approximately 10 μm in the case of high-quality 3C-SiC. The spectra were acquired in the range between 450 and 1700 nm with a cooled InGaAs array detector (Horiba Symphony IGA-512 × 1) utilizing a monochromator Horiba TRIAX 552 (grating: 150 mm⁻¹). All spectra were converted to energy scale by applying Jacobian Conversion.

2.3. Fitting Procedure

PL spectra were analyzed by fitting and approximating the zero phonon lines (ZPL) as well as phonon side bands (PSB) of the involved peaks in the NIR-band and integrating the whole visible range (VIS) band as a measure of total luminescence. It should be noted, that intensity was set to zero if a sample did not show the peak or band under investigation (see, e.g., Figure 1). This was done to avoid falsification of the results due to background intensity from, e.g., adjacent bands that exhibit a temperature dependence as well. All observed bands could be unambiguously identified and the resulting background intensities were significantly lower than the intensities under investigation.

3. Results and Discussion

3.1. Optical Response of Bulk 3C-SiC

The use of sublimation growth for the preparation of 3C-SiC allows the incorporation of a variety of intrinsic and extrinsic defects during crystal growth. In contrast to defects created by irradiation or implantation and subsequent annealing, the evolution history of defects and therefore the final concentration within the 3C-SiC material is different. Nitrogen- (N), boron- (B), and aluminum- (Al) doped freestanding, single crystalline 3C-SiC layers were prepared by epitaxial sublimation growth. In total, 15 samples referred to S1–S15 were characterized within this work. Figure 2 shows a representative set of bulk 3C-SiC samples prepared and investigated within this study.

Raman and X-ray diffraction (XRD) analysis verify that sublimation grown 3C-SiC is of high crystalline quality and quasi stress free. Even though structural defects, especially SFs, still play a role, their density decreases with thickness and saturates below 1000 cm⁻¹ for layers thicker than 175 μm. Figure 3 shows
typical temperature-dependent PL spectra of sublimation grown 3C-SiC samples. Usually, all samples show a band in the VIS and the related second-order diffraction (SOD) of VIS. The intensity of the VIS-band and the related SOD is high for low temperatures and decreases with increasing temperature. The origin of the observed VIS-luminescence was assigned to dopant-related defects such as donor–acceptor pairs and intrinsic defect complexes. Details of both, the VIS and the related SOD, can be found in previous works.[32,33] Samples grown within a limited growth-rate regime (see trend in Figure 1) additionally exhibit a bright band consisting of sharp peaks within the NIR. This band, shown in Figure 3a, increases and subsequently decreases with temperature reaching the maximum at 175 or 200 K. The joint origin of the distinct peaks in the NIR is assumed to be the carbon vacancy \( V_C \).

3.2. Bright Emission in the NIR

Within the NIR-band discrete peaks are apparent (see Figure 4). A weak indication of the NIR-luminescence is already visible at 26 K. With increasing temperature, the NIR-band increases as well until it reaches a maximum at 175 or 200 K, due to the 25 K step size when performing PL analysis. With further increasing temperature, the NIR-luminescence decreases again but remains excitable up to 300 K. Figure 4a shows the dependence of the NIR-band from PL acquisition temperature. Spectra for temperatures below 150 K are not shown as they are influenced by luminescence from the VIS and SOD. In Figure 4b, the maximum of NIR-luminescence is shown for each sample. The diagram indicates that all samples within a limited growth rate regime exhibit the same NIR-band with distinct peaks at the same positions. Altogether, four sharp peaks can be observed with center positions at 1.278, 1.233, 1.171, and 1.138 eV. Sample S7 is presented separately in Figure 4 due to an almost one order of magnitude higher intensity of the 1.171 eV peak. This peak is assumed to originate from an unknown Al-related defect.

3.3. Growth-Rate-Dependent Tailoring of Point Defect Concentration

Figure 1 shows the dependence of the \( V_C \)-peak intensity (Figure 1a) and VIS-band intensity (Figure 1b) on the growth rate of 3C-SiC measured by PL at 175 K/200 K and 26 K, respectively. The intensity of the \( V_C \)-peak is zero for all samples with low growth rates up to 179 \( \mu \text{m} \text{h}^{-1} \) (S2) (see Figure 1a). For samples with growth rates between 203 \( \mu \text{m} \text{h}^{-1} \) (S8) and 270 \( \mu \text{m} \text{h}^{-1} \) (S4)
the VC-peak intensity increases before it starts to drop again for all samples with higher growth rates up to 306 μm/h (S6). Due to the step size (25 K) of PL measurements, the maximum NIR peak intensities are reached for 175 or 200 K. In Figure 1b, the intensity of the whole VIS-band at 26 K shows a stable luminescence for all samples with growth rates up to approximately 243 μm/h (S3). For even higher growth rates, a continuous decrease in luminescence over several orders of magnitude is observed which is assigned to quenching effects.

3.4. Detection of a Novel Al-Related Defect

The sharp peak at 1.171 eV shows a dependence (see Figure 5) on the relative aluminum concentration for 3C-SiC samples that exhibit the bright NIR-band (see Figure 4). The results indicate a clear trend of increasing peak-intensity with increasing relative Al-concentration. Of course, the intensities of the presented samples are also affected by the growth rate and concentration quenching as shown in Figure 1 and 4. However, taking sample S7 as an example, the considerable difference of the height of the 1.171 eV peak is clearly related to Al-concentration. These findings allow to assign this peak to an Al-related defect.

3.5. Discussion

Conclusive results were obtained concerning luminescence from deep-level point defects in 3C-SiC doped with different dopants and dopant concentrations. Not all samples showed the same luminescence behavior but all observed bands could be unambiguously identified. Two bands in the NIR and one band in the VIS were visible. In this work, the luminescence in the NIR was investigated.

First of all, the results are interpreted in relation to literature. Wang et al. observed bright single photon emitters with center wavelengths ranging from 1080 to 1265 nm. The origin of the broad bands was assigned to SFs. This is in accordance with our results as we observed such broad and low intensity bands that might originate from structural defects, probably SFs, as well (see Figure 3c) for samples grown with lower growth rates. In our case, these bands were not limited to a fixed narrow range in the spectra, but were found at different wavelengths within the NIR-region for different samples.

In addition to that, a second NIR-band was observed (Figure 3a). This much more distinct band was of considerable higher intensity and showed four discrete peaks. This band was only present for 3C-SiC material produced with growth rates between 203 and 306 μm/h. According to literature, the discrete NIR-luminescence can be assigned to various VC-related defects. The center wavelengths of these peaks were determined at positions of 1.138, 1.171, 1.233, and 1.278 eV. In literature, there is still a controversy concerning intrinsic point defects and their defect complexes in 3C-SiC. Nevertheless, as a first step, the available data from literature were used for the identification of the peaks. The peak at 1.278 eV is assigned to the VC(+ + ++ ) defect, which is in good agreement with the value from literature of 1.29 eV. The peak at a position of 1.233 eV
is assigned to the carbon–vacancy–antisite pair $V_C\mathrm{C_Si}$ at 1.24 eV.\cite{13} There are no reports in the literature that allow a clear assignment of the peak at 1.171 eV. As this peak is very sharp, it should not originate from structural defects. The luminescence at 1.138 eV can be assigned to the divacancy $V_C\mathrm{V_Si}$, which is in very good agreement with the value of 1.13 eV\cite{17} from literature.

So far, all results were discussed in the context of literature. In the following section, the results will be explained from a crystal growth point of view. As shown in Figure 1a, we observed a growth rate dependent luminescence of $V_C$-related defects. In general, for vapor phase growth methods, an increase of the growth rate is, in addition to pressure, realized by increasing the temperature gradient and/or the absolute temperature at the growth interface. This will increase the driving force for crystallization and therefore induce a faster incorporation of species from the gas phase into the growing crystal. The much faster transport enhances the general probability for incorporation of defects, especially vacancies. Epitaxial sublimation growth of 3C-SiC is moreover performed under Si-rich gas phase conditions,\cite{15} hence offering much more Si gas species than C gas species at the growth interface. Even though this growth condition is necessary to stabilize the cubic polytype during growth, it should further support the incorporation of carbon vacancies. Figure 1 shows the dependence of PL intensity on growth rate for both the NIR-band at 175 K/200 K and the VIS-band at 26 K. Due to the step size of 25 K for the T-dependent PL measurements, the actual intensity maxima for the NIR data points might differ slightly. Nevertheless, the trend for the NIR-luminescence shown in Figure 1a is still reasonable. For low growth rates, no luminescence in the NIR can be observed. The following increase in luminescence is assumed to be directly dependent on $V_C$-concentration. Thereafter, the subsequent decrease in luminescence for even higher growth rates is attributed to concentration quenching\cite{16,17,18} caused by $V_C$-related defects. This hypothesis is supported by the fact that the VIS-band behaves in the same way for high growth rates. While the intensity of the whole VIS-band is stable for growth rates up to approximately 243 $\mu$m h$^{-1}$, the luminescence drops for all samples grown even faster. The evolution of the overall PL intensity is a function of defect concentration. At low defect concentrations, an increase in the number of defects causes an increase of PL yield. However, with increasing number of luminescent centers, the increase of defects causes a decrease in PL intensities. This is due to quenching effects such as nonradiative coupling of luminescent centers at high defect concentrations, also referred to as concentration quenching.\cite{16,17,18}

The appearance of the broad band in the NIR (Figure 3c) should also be discussed in the context of crystal growth. Even if the origin of this band is not yet fully understood, there are indications hinting to structural defects.\cite{19} However, the broad luminescence of lower intensity could also originate from interstitials or both, SF and interstitials.\cite{20,21,22} At this point, the pioneering work of Voronkov\cite{23} should be remembered who established the $V \mathrm{G}^{-3}$ criterion, which describes the growth rate ($V$- and temperature gradient ($G$)-dependent formation of interstitials and vacancies in silicon. A similar effect may be responsible for the growth rate dependent NIR emission in this work. This broad band of lower intensity was only observed for a few samples grown at low growth rate. For low growth rates, the probability for the incorporation of interstitials is higher than for the generation of vacancies. Due to their structure and migration mechanisms, interstitials are more mobile within the crystal lattice than other point defects. In the case of high densities of structural defects, the interstitials can easily move toward structural defects which act as sinks for interstitials. It seems quite reasonable that such clusters of interstitials around structural defects could give rise to broad bands of low intensity as observed in this work.

In Figure 5, the intensity of the peak at 1.171 eV versus the relative Al-concentration is shown. Comparing the trend in Figure 5 with the peak intensities in Figure 4, it is shown that the peak at 1.171 eV increases in intensity and in sharpness with increasing relative Al-concentration indicating a dependency from Al-content. Note that sample S7 with the highest relative Al-concentration cannot be shown in Figure 4 but in the inset therein, due to a much higher intensity of the 1.171 eV peak. Hence, this finding is in accordance with the trend described earlier. All samples that show this intense luminescence were grown within the regime of high $V_C$-concentration (see Figure 1). In the crystal lattice of 3C-SiC, Al preferably occupies the Si-site hinting to an Al-related defect, too.\cite{24} In consideration of the general $V_C$-rich growth regime and the supposed occupation of the Si-site by Al, the $X_S\mathrm{Al}_X$ peak observed is postulated to originate from the $V_C\mathrm{Al}_X$ defect. Of course, this postulation needs to be verified in future works, e.g., by density functional theory (DFT) simulations.

By variation of growth rate, the NIR-luminescence of 3C-SiC can be specifically tailored for individual requirements. To get maximum luminescence intensity, the amount of optically active centers should be as large as possible but should not exceed the critical concentration where concentration quenching becomes relevant. Of course, applications of such point defects are still far away. However, epitaxial sublimation growth can offer a further route for the generation of point defects in addition to irradiation and implantation. As the method of defect generation can directly influence the structure and therefore properties of point defects, this method can at least foster the understanding and development of point defect based applications. Taking quantum computing and qubits as an example, especially the working temperatures are still a limiting factor. As the NIR-luminescence of defects presented in this work exhibited a maximum in the temperature range between 175 and 200 K, this could be a first step toward working temperatures above the cryogenic limit. It has already been demonstrated that $V_C\mathrm{V}_S$ and $V_C\mathrm{C}_S$ can act as single photon sources (SPSs) in SiC\cite{25,26}. Therefore, even if further steps like isolation of single defects for SPS will be necessary to realize applications, $V_C$-related defects as presented in this study should be considered for further investigations on applicability for quantum devices.

4. Conclusion

In conclusion, we present the luminescence of various defects in the NIR-region. The principal defect, as essential for the occurrence of all observed defects, is assumed to be the carbon vacancy. Therefore, the whole NIR-band reveals a growth rate dependence that can be very well explained by inherent growth conditions, i.e., the driving force for crystallization and the gas phase composition.
during epitaxial sublimation growth. For the first time, the controlled incorporation—according to probability and density—of deep-level defects during epitaxial sublimation growth of high-quality bulk 3C-SiC is presented. In addition, it is shown that in situ doping can open up further opportunities for defect engineering. By variation of the aluminum content, the intensity of an Al-related defect could be changed by more than one order of magnitude.

Controlled incorporation of deep-level defects in 3C-SiC, defect engineering through doping and bright luminescence at temperatures around 175 K/200 K can help to bring 3C-SiC-based applications within tangible reach.

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Conflict of Interest
The authors declare no conflict of interest.

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