Investigation of deep electronic levels in n-type and p-type 3C-SiC using photoluminescence

Martin Wilhelm\textsuperscript{1}, Mikael Syväjärvi\textsuperscript{2}, Peter J. Wellmann\textsuperscript{1}\textsuperscript{*}

\textsuperscript{1}Crystal Growth Lab, Materials Department 6 (i-meet), University of Erlangen-Nürnberg (FAU), Martensstr. 7, 91058 Erlangen, Germany
\textsuperscript{2}Department of Physics, Chemistry and Biology (IFM), Linköping University, 51883 Linköping, Sweden

*Corresponding author; Tel: (+49) 9131-8527635, E-mail: peter.wellmann@fau.de

Received: 05 September 2017, Revised: 06 September 2017 and Accepted: 30 September 2017

DOI: 10.5185/amp.2017/415
www.vbripress.com/amp

Abstract
Among the various SiC polytypes, cubic 3C-SiC is much more difficult to grow in high crystalline quality than the commercially introduced hexagonal 6H-SiC and 4H-SiC counterparts. Besides some benefits of 3C-SiC for transistor applications related to a greater electron mobility and a lower metal-oxide-semiconductor interface trap density compared to 4H-SiC, new potential optoelectronic applications have been introduced very recently. Boron doped 3C-SiC may act as an ideal candidate for an intermediate band (IB) solar cell material. Aluminum doped p-type 3C-SiC could lead to the development of efficient optoelectrochemical water splitting cells. Finally, 3C-SiC with its various intrinsic point defects has been considered as a suitable candidate for future spintronic-applications. All these applications will critically depend on further understanding defect behaviour on atomic level. In our study we investigated free standing n-type and p-type 3C-SiC material grown in our lab. Temperature dependent photoluminescence measurements revealed the presence of carbon vacancy related $V_C$ and $V_C-C_S$ defect transitions in the p-type materials but not in the n-type materials. This observation present in as grown 3C-SiC is believed to have significant impact on the optoelectronic applications. Copyright © 2017 VBRI Press.

Keywords: 3C-SiC, doping, p-type, defects, carbon vacancy.

Introduction
In recent years, SiC has gained much interest as a semiconductor material for energy saving applications. Its unique physical properties like great break down field, great electron saturation velocity and great heat conductivity make it superior over silicon in the case of power electronic devices. For an overview on the growth of SiC boules see e.g. [1-6]. Other applications of SiC make use of its superior radiation hardness (X-ray and g-ray detectors), chemically inertness (biomedical coatings) and very low nuclear magnetic moment (spintronic) [7-11].

The cubic 3C-SiC is known to be much more difficult to grow in high crystalline quality than the hexagonal 6H-SiC and 4H-SiC counterparts. The 3C-SiC is more attractive in certain transistor applications related to a greater electron mobility and a lower metal-oxide-semiconductor interface trap density compared to 4H-SiC. More importantly for energy applications, the p-type doping by B and Al presents interest in new optoelectronic applications, the combination of suitable bandgap and high electron mobility in 3C-SiC together with the almost perfect deep level position of B make 3C-SiC an ideal candidate for an intermediate band (IB) solar cell material [12-13]. Aluminum doped p-type 3C-SiC reduces the oxidation of 3C-SiC and could allow development of efficient opto-electrochemical solar driven water splitting cells for hydrogen generation [13-15]. Prospectively, 3C-SiC with its various intrinsic point defects is very promising for future spintronic quantum computing applications [7,11]. All these activities are supported by a continuous progress in the growth of quasi bulk cubic SiC (see e.g. [17-21]).

In this study we have prepared freestanding n-type and p-type 3C-SiC material. Temperature dependent photoluminescence measurements is well known as an established tool to explore SiC properties, and suitable to distinguish intrinsic point defects in the n and p-type material. It is particularly useful in case of potential spintronic applications, and it is noteworthy that the studied point defect occurs in as grown p-type 3C-SiC rather than being formed using implantation techniques [7,11].
Experimental

The n-type and p-type freestanding 3C-SiC samples of 10 mm x 10 mm in size (thickness 200 µm to 500 µm) were grown on (0001)-oriented 6H-SiC wafer pieces (Si-face) under Si-rich gas phase conditions using the sublimation sandwich method [17,19,21]. Polycrystalline SiC bulk wafers prepared in the own lab were applied as SiC source material [22]. Details of the growth setup and the growth parameters to enforce a polytype change to 3C-SiC during seeding and to constrain the latter during continuous growth are reported elsewhere [20,23].

Doping type and doping level of the 3C-SiC material, i.e. n-type versus p-type, was varied by the choice of the doping of the poly-SiC source material. For this purpose, the SiC source material was fabricated using the addition of nitrogen gas (ca. 8 sccm and 9 sccm nitrogen gas) for n-type doping and boron doping (50 ppm boron) for p-type doping [22].

Al doping is more challenging due to the reactive character with graphite and source, but we have achieved p-type material by using Al contamination of the originally applied SiC powder source from which the poly-SiC source materials have been fabricated. Fig. 1 depicts optical images of the investigated 3C-SiC samples and summarizes their chemical doping levels.

Temperature dependent photoluminescence (PL) measurements were performed between T = 22 K and 300 K. As excitation sources we used laser diodes at 405 nm (above band gap excitation) and 662 nm (below band gap excitation). The laser power varied between 1 mW and 100 mW. Visible luminescence in the spectral range between 450 nm and 900 nm was detected using a cooled silicon CCD-array detector. Near infrared light in the spectral range from 900 nm to 1700 nm was acquired by a cooled InGaAs line detector. Fig. 2 shows PL spectra of the n-type and p-type 3C-SiC samples measured at T = 22K.

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**Fig. 1.** Optical images and doping parameters of the investigated 3C-SiC samples.

- sample 1, n-doped
  - 50 ppm B, 9 sccm N
  - B: 1,12·10^{18} cm^{-3}
  - Al: 1,27·10^{18} cm^{-3}
  - N: 7,74·10^{18} cm^{-3}

- sample 2, p-doped
  - 50 ppm B, 8 sccm N
  - B: 1,4·10^{18} cm^{-3}
  - Al: 1,38·10^{18} cm^{-3}
  - N: n.a.

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**Fig. 2.** PL spectra of an n-type (a) and a p-type (b) 3C-SiC sample measured at T = 22K.

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**Fig. 3.** Band diagram energetic position of dopants of 3C-SiC.
Results and discussion

Fig. 4 depicts the T dependence of the bandgap and donor-acceptor related as well as deep level photoluminescence of p-type 3C-SiC. The increase of the temperature from 22 K to 300 K goes along with a drop of the bandgap and donor-acceptor related luminescence intensity due to a simultaneous increase of non-radiative charge carrier recombination.

![Image of Fig. 4](324x574 to 558x703)

*Fig. 4. Temperature dependent donor to acceptor pair luminescence showing indication of deep transitions.*

The conduction band / nitrogen donor to valence band transition at 550 nm (22 K) smoothly shifts to a pure conduction to valence band transition at 540 nm (300 K). The pronounced luminescence of the conduction band / nitrogen donor to shallow aluminum, shallow boron and deep boron acceptor transition observed at 22 K significantly drops and almost vanishes when increasing the temperature up to room temperature.

Interestingly, with increasing temperature deep level luminescence around 1000 nm is observed which may be related to optical transitions of carbon-vacancy V_C and carbon-vacancy carbon antisite V_C-C_Si defects. To investigate the occurrence and properties of intrinsic defects as a function of doping type, i.e. n-type versus p-type 3C-SiC, we have studied the temperature dependence of the near infrared luminescence between 800 nm and 1400 (Fig. 5) for all samples presented in Fig. 1.

The n-type 3C-SiC (sample 1) shows a broad optical transition band between 900 and 1200 nm, however, with no special features that may be related to distinct point defects (Fig 5a). In the case of p-type 3C-SiC (samples 2) three pronounced luminescence transition are observed at 970 nm (1.28 eV), 1005 nm (1.23 eV) and 1058 nm (1.17 eV) as well as two shoulder-like features at 1085 nm (1.14 eV) and 1150 nm (1.08 eV) (Fig. 5b, Table 1).

Using ab initio calculations based on density functional theory, Bockstedte et al. [24] have calculated the electronic charging energies of various point defects of carbon vacancy type. The electronic transitions at 970 nm (1.28 eV), 1005 nm (1.14 eV) and 1058 nm (1.23 eV) shown in Fig. 5b may be related to V_C and V_C-C_Si defect luminescence (see Table 1). The 970 nm (1.28 eV) luminescence exhibits a temperature dependence of its luminescence intensity against expectation. Other than the continuous drop of the bandgap and donor-acceptor related luminescence with increasing temperature, the V_C (+/+)-transition at 970 nm starts to evolve above 140 K (regime 2 in Fig. 6) featuring a maximum signal at 220 K and a subsequent drop towards room temperature (regime
3 in Fig. 6). The \( V_C (++) \) state is stable at Fermi energies below 1.3 eV with the valence band as energetic 0 eV reference [24,25]. Because of the great acceptor ionization energies of the intentional boron and unintentional Al doping in 3C-SiC compared to the nitrogen donor (see table inset in Fig. 2), a reasonable shift of the Fermi energy into the underpart of the bandgap towards the valence band takes place above \( T = 140 \) K. Hence, solely an unspecified background luminescence is observed at 970 nm (1.28 eV) for \( T < 140 \) K (regime 1 in Fig. 6).

![Fig. 6. Temperature evolution of the luminescence intensity of the 970 nm (1.28 eV) \( V_C (+++) \) defect transition.](image)

Due to the theoretical considerations of Gordon et al. [26] the 1085 nm (1.14) luminescence shoulder in Fig. 5b could also be assigned to a divacancy \( V_C-V_S \) transition at 1.12 eV that is of particular interest for quantum computing applications [7,11,26].

Bockstedte et al. [24] pointed out that the electronic charging of the carbon vacancy \( V_C \) defect states exhibits a strong electron phonon coupling. Considering a LO-phonon energy of 102.8 meV in 3C-SiC [27], the electronic transitions at 1058 nm (1.17 eV) and 1150 nm (1.08 eV) in Fig. 5b could be interpreted in terms of phonon replica of the 970 nm (1.28 eV) luminescence. However, the incoherence in temperature dependence suggests that the 1058 nm (1.17 eV) and 1150 nm (1.08 eV) transitions are not related to a \( V_C \) defect. Therefore, the final assignment to carbon vacancy \( V_C \) related defects remains unclear.

**Conclusion**

The p-type 3C-SiC semiconductor exhibits a number of electronic carbon vacancy \( V_C \) related defect luminescence transitions in the near infrared between 970 nm (1.28 eV) and 1150 nm (1.08 eV) which are not present in n-type 3C-SiC. Therefore, p-type 3C-SiC is a hot candidate for novel optical applications. Clearly, the details of these complex defects will be strongly influencing the optoelectronic behavior.

**Acknowledgements**

This work was supported by the STAEDTLER-Stiftung (Germany) under contract number WW/eh 13/15. Technical assistance to carry out photoluminescence measurements and literature studies by Florian Barton in the frame of a bachelor thesis is greatly acknowledged.

**Author’s contributions**

Conceived the plan: MW, MS, PW; Performed the experiments: MW; Data analysis: MW, MS, PW; Wrote the paper: PW. Authors have no competing financial interests.

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DOI: 10.1021/acscgd.5b00368
DOI: 10.1002/pssa.201600429