# Theoretical study of defects in silicon carbide and at the silicon dioxide interface

PH.D. THESIS

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# Introduction

Silicon carbide (SiC) is a wide band gap semiconductor, and one of the best candidates for compact, low-loss, high-temperature and high-power electronic devices. Carbon (C) and its strong bonds to silicon (Si) ensure much higher breakdown voltage and better heat conductivity than that of pure silicon. However, the presence of carbon introduces a number of problems which require changes in processing technology and additional materials science knowledge: understanding crystal defect properties greatly contributes to the optimization of manufacturing technology. Due to the strong carbon-silicon bonds there are only two possible ways of SiC doping: implantation and in-growth doping from the gas phase by dopant containing precursors. During implantation several crystal defects are created: vacancies, interstitials and anti-sites, which can form electron or hole traps by deep levels in the band gap reducing the lifetime and the concentration of free carriers. A subsequent heat treatment is used to restore the desired crystal structure and activate the dopants. However, defects with traps that adversely influence the carrier concentration can still remain thereafter.

It is of high importance to study the role of these defects by electronic structure calculations, that can provide specific defect models for experiments in order to identify the unknown defect centers. In my Ph.D. work I studied defects formed by common $n$- and $p$-type dopants of SiC as well as clusters of carbon and silicon self-interstitials. I also investigated the nitridation of the SiC/SiO$_2$ interface traps with *ab initio* supercell calculations. The latter work took place in the Bremen Center for Computational Materials Science at the University of Bremen and was funded by a DAAD short term research scholarship. The former three investigations were done at the Department of Atomic Physics at Budapest University of Technology and Economics. Electronic structure calculations were performed on various clusters and supercomputers in Hungary and abroad. I also did modifications and improvements of simulation codes and developed several programs for data analysis as well as built the computing cluster at the department.

# Goals of the research

Phosphorus (P) is one of the common $n$-type dopants of SiC. Theory predicts that the solubility of the shallow P-donor can reach the $10^{21}$ cm$^{-3}$ range limit for high temperature growth [1]. However, the maximum measured concentrations of P-donors is at about $10^{17}$ cm$^{-3}$ in physical vapor transport growth [2]. Wang and co-workers introduced phosphorus into SiC during chemical vapor deposition (CVD) growth by supplying P-containing precursors [3]. They found that the maximum carrier concentration did not exceed $10^{17}$ cm$^{-3}$ for any set of growth conditions. They also found that the P-donor concentration did not show clear site-competition effect moreover at high carbon/silicon (C/Si) ratio the concentration of P-donors was even lower than at lower C/Si ratio. It was speculated that hydrogen (H) can influence the

site selection of phosphorus as in the case of boron, thus explaining the unexpected behavior of P-donors [3]. I calculated the electronic structure and the concentration of various P-related defects ($P_{Si}$, $P_C$, $P_{Si} + H$, $P_C + H$ and P pairs), which are relevant during the CVD growth of SiC to explain the above mentioned experimental results.

Aluminum (Al) is one of the common $p$-type shallow acceptor [4] dopant of SiC. It is introduced into the crystal by implantation. Deep level transient spectroscopy (DLTS) and electron paramagnetic resonance (EPR) measurements revealed several shallow and deep Al-related centers [5–7] even after annealing at 1700 °C [8]. In irradiated SiC mobile carbon interstitials were also created. Theoretical calculations showed, that aggregation of carbon and boron interstitials are very feasible processes [9, 10]. Similar complex formation of aluminum and carbon self-interstitials can occur in Al-implanted SiC. I investigated the complexes of aluminum with carbon interstitials and the carbon vacancy in order to explain the origin of the Al-related centers in $4H$-SiC. I calculated the electronic structure, occupation levels and binding energy of the defects.

During implantation carbon ($C_i$) and silicon ($Si_i$) self-interstitials are also created. Experimental findings and theoretical calculations [11] showed, that silicon interstitials play an important role in implanted or irradiated SiC. Photoluminescence (PL) measurements showed, that there are Si-related defects even after annealing, among which the most important and disputed defects are the alphabet lines [12, 13] and the $D_I$ center [12, 14–19]. I studied the isolated silicon interstitial and the small clusters of $Si_i$ and $C_i$ by *ab initio* supercell calculation in $4H$-SiC in order to clear the role of silicon-related clusters. I calculated the electronic structure, occupation levels and binding energy of the defects, as well as local vibration modes.

Silicon carbide possesses the great advantage of having silicon dioxide ($SiO_2$) as its native oxide that is essential for SiC-based metal-oxide-semiconductor devices. Unfortunately, the usual thermal oxidation produces an unacceptably high density of interface states ($D_{it}$). Deep states are assumed to be caused by carbon excess at the interface, while the slow electron traps, called NITs (near interface traps), are expected to originate from oxide defects near the interface. Simple hydrogen passivation does not help to reduce the high trap density [20]. Substantial improvement, however, can be achieved by nitridation, either through oxidation [21–23] or post-annealing [22–27] in the presence of nitrogen (N). Previous theoretical investigations showed, that the dominant part of the $D_{it}$ cannot be explained by simple intrinsic defects. Slow electron traps (NITs) are carbon dimers ($C_O = C_O$) in the oxide, while deep states are the carbon-related defects ($C_i = C_i$ and $(C_i)_C$) near the interface region [28, 29]. I investigated the nitrogen passivation of these carbon-related defects at the SiC/$SiO_2$ interface by *ab initio* supercell calculations in order to clarify the effects of atomic N and the NO molecule on carbon-related interface defects. I calculated several nitrogen-related interface defects to determine the occupation levels and the reaction energies. Based on the results I investigated

the possible reaction mechanisms of the nitrogen passivation of carbon-related defects at the $4H$-SiC/SiO$_2$ interface.

# New scientific results

## 1. Doping of phosphorus in chemical-vapor-deposited SiC layers

(a) I showed, that the most abundant P-related defect is the shallow donor ($P_{Si}$) with a maximum concentration of $10^{17}$ cm$^{-3}$ under typical CVD growth conditions. The second most abundant defect is the $P_C$ defect, a sightly deeper donor, at least one and a half orders of magnitude less concentration than that of the $P_{Si}$ defect. The difference of defect formation energies does not depend on the chemical potential of phosphorus, thus the concentration difference should be valid for any condition of CVD growth, which is close to a quasiequilibrium process. I showed, that the concentration of other P-related defects ($P_{Si}$ + H, $P_C$ + H and P pair) are much smaller, below $10^{10}$ cm$^{-3}$, therefore, only the $P_{Si}$ defect contributes significantly to the concentration of free carriers in P-doped epitaxial SiC layers. [T1, T6]

(b) I showed, that the most stable configurations for hydrogen (atoms) in the $P_{Si}$ + H and $P_C$+H defects are behind P atoms at antibonding positons. Both complexes are electrically inactive possessing no levels in the band gap of $4H$-SiC. The calculated binding energies of the hydrogen interstitial ($H_i^-$) to the $P_{Si}^+$ and $P_C^+$ defects are about 0.3-0.5 eV and 0.1-0.3 eV, respectively, which indicates that both complexes dissociate at relatively low annealing temperature. Therefore, I predicted that no passivation effect is expected by hydrogenating the P-donors. [T1, T6]

(c) I proposed a model to explain why the site-competition effect does not work for phosphorus in CVD growth and explained the unexpected behavior of P-dopants on the applied C/Si ratio by the change of the chemical potential of phosphorus: at higher C/Si ratio more Si vacancies are produced promoting the formation of the $P_{Si}$ defects. However, this effect can be compensated by the change in the chemical potential of phosphorus via the additional hydrogen content provided by $C_3H_8$ molecules. As a consequence, the concentration of the $P_{Si}^+$ defect–and that of the free carriers–can be, indeed, lower at higher C/Si ratio. [T1, T6]

## 2. Aluminum-related defects in $4H$-SiC

(a) I found that the aluminum acceptor ($Al_{Si}$) may form a stable complex with two carbon interstitials and certainly forms a stable complex with the carbon vacancy with a binding energy of 5.8 eV and 0.5 eV (the diffusion barrier of the carbon vacancy is about 4 eV), respectively. I also found that aluminum interstitial forms stable and metastable complexes with one or two carbon interstitial(s). All these defects produce deep levels in the band gap of $4H$-SiC. I found, that in heavily Al-implanted regions also the $Al_{Si}(C_i)_2$ defect may be created as well, that is a thermally very stable defect possessing a deep level at about $E_V$ + 1.3 eV. Therefore, I showed

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that this defect could be one of the reasons of the imperfect activation rate of the shallow Al acceptor. [T2, T7]

(b) Based on my results I clearly rule out Matsuura's model ($Al_{Si}V_C$) [30] for the new Al-related center at $E_V + 0.37$ eV. The calculated occupation levels of the $Al_{Si}V_C$ defect are at about $E_V + 1.5$-$1.6$ eV. These levels are, however, very close to the measured DLTS level of trap A3. The activation energy of trap A3 was estimated to be around $1.70 \pm 0.1$ eV showing a big bump in the DLTS spectrum [8]. I propose the $Al_{Si}V_C$ defect an appropriate candidate for the trap A3 DLTS center. The broad bump of the A3 signal can be explained by the unresolved $(+/0)$ and $(0/-)$ levels. I showed that this defect could also be one of the reasons of the imperfect activation rate of the shallow Al acceptor. [T2, T7]

(c) I also calculated the binding energies and occupation levels of stable and metastable defects of aluminum and carbon interstitials. The $(2+/+)$ and $(3+/2+)$ levels are at around $E_V + 1.2$ eV. I propose that this defect may be the source of the A1 and A2 DLTS centers at $E_V + 0.82$ eV and $E_V + 1.02$ eV, respectively. However, the calculated binding energy of the $Al_iC_i$ defect (1.9 eV) does not clearly explain the high termal stability of these traps. Additional information about the nature of A1 and A2 traps [8] is needed in order to identify them. I showed that this defect can capture an additional $C_i$ and form the thermally, even up to 1700 °C, very stable $Al_i(C_i)_2$ defect. [T2, T7]

**3. Small silicon clusters in 4$H$-SiC**

(a) I investigated the isolated $Si_i$ defect by *ab initio* calculations in 4$H$-SiC for the first time. I showed, that in $p$-type 4$H$-SiC the $Si_i$ is in the 4+ charge state at an empty place caged by four carbon atoms similar as in 3$C$-SiC. I found that in $n$-type 4$H$-SiC the $Si_i$ is neutral. In the most stable configuration the $Si_i$ is in a split-interstitial position at a cubic site with $C_{1h}$ symmetry. I found a different structure for the $Si_i$ at the hexagonal site, where it is at an empty place caged by carbon atoms. This hexagonal-caged structure is about the same stability as the cubic configuration. I found that both structures have deep levels in the gap localized around the silicon interstitial. The hexagonal-caged configuration exhibits a negative-U property with $(2+/0)$ occupation level at $E_V + 2.3$ eV. [T4, T9]

(b) I investigated the smallest aggregates of Si interstitial related clusters. I found two stable (cubic and hexagonal) and four metastable configurations. The cubic structure is more favorable than the hexagonal one. Both defects are electrically active and have four occupied levels in the band gap of 4$H$-SiC, mostly localized on the $Si_i$ atoms. Based on the calculated binding energies I estimated the annealing temperature of these defects, which is between 1000 °C and 1300 °C. As a result,

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I prove that $Si_i$ is emitted from such silicon-related clusters and involved in the formation of the $D_I$ PL center that is starting to be generated at above 1000 °C. [T4, T9]

(c) In order to help the experimental identification of these defects I also calculated the local vibration modes. Several new modes appeared in the phonon gap due to the $Si_i$-$Si_i$ bond. I identified those modes which are coupled with a PL process based on group theory. I predicted that lines in the calculated phonon gap and above the calculated phonon band can be detected by PL measurements. Later, PL centers have been indeed detected by Prof. Steeds that may be associated with the calculated defects [31,32]. [T4, T9]

(d) I investigated the simplest structures with one carbon and one silicon interstitial. I found one stable and six metastable configurations. The most stable structure contains $Si_i$ and $C_i$ at the hexagonal site. The calculated binding energy is at about 4.3 eV, which predicts high thermal stability for this defect. I found that this defect is electrically active with deep levels in the band gap of $4H$-SiC, strongly localized on the $C_i$ and $Si_i$ atoms and their first neighbor atoms. It has a negative-U property with a $(2+/0)$ occupation level at $E_V + 2.0$ eV. I propose that this defect can also be formed in irradiated $4H$-SiC. In order to help the identification by PL measurements I provided the occupation levels and local vibration modes also for the $^{13}$C isotope substitution of the carbon atoms. [T4, T9]

4. **Nitrogen passivation of traps at the SiC/SiO$_2$ interface**

(a) I found that there are two competing processes of the dissociation of NO molecules near the interface. I showed that the dominating reaction is the creation of interstitial nitrogen at the interface ($N_{if}$) by releasing oxygen interstitial ($O_i$) into the oxide. The less dominating reaction is the nitrogen doping of the interface (in the form of the $N_C$ defect) by releasing a CO molecule into the oxide. In the considered Fermi energy range the energy gain of these reactions are 3.0-3.9 eV and 2.6-2.9 eV, respectively. [T5, T10]

(b) I showed that NO molecules can interact with the carbon dimers at the interface. In the dominant reaction nitrogen gets incorporated in a nitrogen-carbon dimer ($N_i = C_i$) by releasing a CO molecule into the oxide. In the less dominant reaction it produces interface oxygen and carbon interstitial by releasing a CN molecule into the oxide. I showed that in the considered Fermi energy range these reactions have the energy gain 3.7-4.0 eV and 2.5-3.1 eV, respectively. Based on my results I showed that both reactions prevent the formation of carbon dimers at the interface, therefore the carbon dimers cannot act as NITs in the oxide. I also showed, that atomic nitrogen from a dissociated NO molecule can also attack carbon dimers

either by nitrogen incorporation or by carbon interstitial production similarly as in the case of the NO molecule. The calculated energy gains are 1.6-1.9 eV and 1.4-1.7 eV, respectively. Based on these results, I explained why nitrogen plasma treatment or nitrogen implantation prior to oxidation also removes carbon dimers at the interface. [T5, T10]

(c) I showed that interface oxygen ($O_{if}$) produced by the dissociation of the $O_2$ molecule can be attacked by the NO molecule and also by the $N_i$ defect and complete a stoichiometric oxidation of the interface releasing a CN into the oxide. The calculated energy gain is around 3.5 eV. Based on these results I explained the ultimate benefit of nitridation: nitrogen, in conjuction with the $O_2$ molecule, can complete a stoichiometric oxidation sequence removing the resulting carbon atoms from the interface altogether, before those could form the carbon dimers in the first place. [T5, T10]

# Refereed papers related to the thesis

[T1] **Doping of phosphorus in chemical-vapor-deposited silicon carbide layers: A theoretical study**
*T. Hornos, A. Gali, R. P. Devaty, and W.J. Choyke*
Appl. Phys. Lett. **87** 212114 (2005)


[T2] **Ab initio supercell calculations on aluminum-related defects in SiC**
*A. Gali, T. Hornos, N. T. Son, E. Janzén, and W. J. Choyke*
Phys. Rev. B **75** 045211 (2007)


[T3] **Activation of shallow boron acceptor in C/B co-implanted silicon carbide: A theoretical study**
*A. Gali, T. Hornos, R. P. Devaty, N.T. Son, E. Janzén, and W.J. Choyke*
Appl. Phys. Lett. **86** 102108 (2005)


[T4] **Theoretical Study on Silicon-clusters in SiC**
*T. Hornos, N. T. Son, E. Janzén, and A. Gali*
Phys. Rev. B **76** 165209 (2007)


[T5] **The mechanism of defect creation and passivation at the SiC/SiO$_2$ interface**
*Péter Deák, Jan M. Knaup, Tamás Hornos, Christoph Thill, Adam Gali and Thomas Frauenheim*
J. Phys. D **40** 6242-6253 (2007)

# Refereed conference papers related to the thesis

[T6] **A Theoretical Study on Doping of Phosphorus in Chemical Vapor Deposited SiC Layers**

*T. Hornos, A. Gali, R. P. Devaty, and W.J. Choyke*

Mater. Sci. Forum **527-529** 605-608 (2006)


[T7] **A Theoretical Study on Aluminum-Related Defects in SiC**

*T. Hornos, A. Gali, N. T. Son, E. Janzén*

Mater. Sci. Forum **556-557** 445-448 (2007)


[T8] **Point Defects and Their Aggregation in Silicon Carbide**

*A. Gali, T. Hornos, M. Bockstedte, T. Frauenheim*

Mater. Sci. Forum **556-557** 439-444 (2007)


[T9] **New Type of Defects Explored by Theory: Silicon Interstitial Clusters in SiC**

*A. Gali, T. Hornos, N. T. Son, and E. Janzén*

Mater. Sci. Forum **600-603** 413-1416 (2009)


[T10] **The Mechanism of Interface State Passivation by NO**

*P. Deák, C. Thill, J. Knaup, T. Frauenheim, T. Hornos, A. Gali*

Mater. Sci. Forum **556-557** 541-544 (2007)

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