Irradiation-induced crystal defects in silicon carbide

Summary of the Ph.D. thesis

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Introduction

Electronics has a major impact on everyday life and today's society. Increasing demands for smaller electronic devices with improved performance at lower costs drove conventional silicon-based microelectronics technology to its limits. To satisfy requirements from industry and to extend applications of semiconductor devices, new materials and fabrication techniques have to be used.

At an early stage germanium (Ge) was mainly used as the semiconductor material, but eventually silicon (Si) achieved lead in semiconductor processing due to the relative ease to produce high quality crystals. Since the 1980s, the interest in the development of wide bandgap materials has increased drastically, as their unique physical properties make them very attractive for high-temperature, high-power and high frequency application fields, where the requirements are beyond the limits of Si technology. One of the most promising wide bandgap semiconductor is silicon carbide (SiC) with high electron mobility, high breakdown field, high saturated electron drift velocity, and high thermal conductivity [Harris, 1995]. Moreover, the small cross-section for interaction with neutrons, low activation under neutron irradiation, good thermal conductivity, and high thermal and mechanical stability lead to its potential use in structural components for fusion reactors, even as cladding material for gas-cooled fission reactors.

Objectives

A number of problems in the development of any crystalline semiconductor are tightly connected with the understanding of defects in the material. Defects can trap free carriers, influence carrier generation and recombination and reduce the carrier lifetime, or act as scattering centers to limit the mobility. Defects can be found already in as-grown crystals, but are also formed during common device processing steps, such as ion implantation, irradiation and etching. They can migrate and anneal at high temperatures, or sometimes can transform into complexes. Usually defects are associated with harmful effects on device operation, but this is not always the case – short lifetimes are sometimes required for fast-switching diodes, and also, semi-insulating material for substrate applications is impossible to realize without deep level defects. The investigation of electronic and magnetic properties of point defects in order to understand their role in device operation is an important task.

In SiC, because of the binary compound nature and its crystalline structure giving rise to different inequivalent lattice sites (2 in the 4H and 3 in the 6H polytype) a large variety of defects exist. This condition makes defect studies rather complicated. To date only few defect centers have been unambiguously identified and characterized in SiC using the combination of different electrical, magnetic, or spectroscopic characterization techniques.

Another problem with SiC is doping. Contrary to the conventional Si-based semiconductor technology, the doping of SiC cannot be performed by thermal diffusion because of very low diffusion coefficients of dopants [Zetterling, 2002]. Due to this limitation ion implantation to high fluences is the only accessible selective area doping technique for SiC. However, ion bombardment leads to the formation of structural defects, and the final defect composition depends on factors like ion mass, fluence, fluence rate, temperature, and the orientation of the ion beam with respect to the crystallographic axes of the target. Damage accumulation leads to deactivation of dopants through defect-dopant interactions [D. Åberg *et al.*, 2001; U. Gerstmann *et al.*, 2003] and also to amorphization of the material [Jiang *et al.*, 2004]. The high thermal stability of SiC is in this sense a disadvantage since implantation produces some high temperature stable defects. These will be very difficult to remove, by annealing, once they are created. The understanding of the irradiation-induced crystalline-to-amorphous phase transition and its possible re-crystallization by post-implantation annealing is of major concern. The main goal is to minimize the amount of implantation-induced defects at a certain fluence of dopant atoms.

The aim of my Ph.D. work is to contribute to the identification and characterization of electron-irradiation induced point defects in SiC and to provide understanding on the accumulation of disorder induced by implantation of nitrogen (N) and aluminum (Al) ions – the commonly used n- and p-type dopants in SiC.

Experimental methods

The thesis is divided into two parts. The first part deals with the measurement of electronic/magnetic properties and the thermal stability of silicon vacancy-, carbon vacancy-, and carbon vacancy-carbon antisite related defects in SiC. The applied experimental technique is continuous-wave X-band electron paramagnetic resonance (EPR) and photoexcitation-induced electron paramagnetic resonance (photo-EPR). EPR allows to study the spin state and electronic structure of defect centers, the symmetry properties of point defects as well as the chemical identification of the neighbor atoms surrounding the defects. In addition, with the photo-EPR technique the charge state of the defect can be changed by adding electrons to or removing electrons from the defect using light illumination. Photo-EPR also enables to gain information about the excited states of point defects. Major part of my work was done at the Institute of Physics and Measurement Technology (IFM) at Linköping University in Linköping, Sweden.

In the second part of the thesis, the disorder accumulation as a function of the implantation fluence and/or the direction of the bombarding N or Al ions with respect to the <0001> crystallographic axis of SiC is discussed. A widely used experimental technique to measure the implantation-induced disorder in single crystalline solids is Rutherford Backscattering Spectrometry in combination with channeling technique (RBS/C). Usually the method operates with a $^4He^+$ analyzing ion beam in the energy range 1-2 MeV. In conventional RBS/C the Rutherford cross-section of He ions for the target C atoms is about seven times lower than for the target Si atoms, so that only the Si sublattice of SiC can be investigated. In this thesis a unique case of the ion backscattering technique is applied: 3.5 MeV $^4He^+$ backscattering in combination with channeling (BS/C). At this energy the cross-section for C exceeds the Rutherford value by about a factor of six and the method yields information simultaneously from both the Si and C sublattices of SiC with good sensitivity and good depth resolution for quantitative analysis of the depth distribution of disorder. The ion implantation and the ion backscattering experiments have been done at the Research Institute for Technical Physics and Materials Science and at the Research Institute for Particle and Nuclear Physics of the Hungarian Academy of Sciences in Budapest, Hungary.

New scientific results

1. I have studied the annealing behavior of the EI5 and EI6 centers in electron-irradiated p-type 4H-SiC by electron paramagnetic resonance (EPR). EI5 was previously attributed to the positively charged carbon vacancy at the cubic lattice site, whereas EI6 was correlated to the positively charged silicon antisite. I followed the EPR intensity of the hyperfine (HF) lines of the centers both with and without light illumination between room temperature and 1600 °C annealing.
   a) Concerning the EI5 center, I have shown that the intensity change due to the change in the charge state of the defect may interfere with the intensity change due to the annealing of the defect. The HF lines of the center were still present after a 1350 °C anneal showing much higher thermal stability of the carbon vacancy than that previously reported [1].
   b) I found that the annealing behavior of the EPR intensity of the EI6 center is similar to that for the EI5 center both with and without light illumination. Consequently – contrary to its previous identification – I proposed the EI6 center to be related to the positively charged carbon vacancy at the hexagonal lattice site of 4H-SiC [1].

2. I have identified the P6/P7 EPR centers in electron-irradiated 4H-SiC. I found four different spectra with the electron spin S = 1, two of them have C_{3V} symmetry (P6a,b) and the remaining two have C_{1h} symmetry (P7a,b). I analyzed the angular dependence of the spectra in the $[11\bar{2}0]$ rotation plane of 4H-SiC. The g and D tensor parameters, the symmetry, and the correspondence between the number of spectra and the number of inequivalent lattice sites in 4H-SiC have confirmed that the P6a,b centers are related to the carbon vacancy–carbon antisite (V_C–C_{Si}) pairs oriented along the c-axis and located at the cubic and hexagonal lattice sites of 4H-SiC, whereas P7a,b are also related to V_C–C_{Si} defects but are oriented along the other three tetrahedral bonding directions, respectively. I found that the annealing behavior of the P6/P7 centers in irradiated material confirms the theoretical calculations predicting the transformation of the Si vacancy into the V_C–C_{Si} pairs at elevated temperature [2].

3. I have detected the EPR spectrum of the T_{V2a} center in as-grown semi-insulating (SI) 4H-SiC grown by high-temperature chemical vapor deposition (HTCVD) in the absence of the EPR signal of the negatively charged silicon vacancy, V_{Si}^-. In my experiment the T_{V2a} spectrum with only two lines was detected. This argument, together with the results of previous Zeeman studies showing the nonsplitting of the photoluminescence (PL) zero phonon line of T_{V2a} confirm the spin S = 1 of the

center. Based on photo-EPR experiments I have concluded that the T_{V2a} spectrum arises from a triplet ground state and has a singlet excited state. I used this model to explain the origin of the associated PL line of the center by a radiative transition from the singlet excited state to the |1,0> singlet sublevel of the triplet ground state [3].

4.
   a) I have studied the disorder accumulation in 4H-SiC induced by 3.5 MeV He ions during backscattering spectrometry/channeling (BS/C) measurements. The disorder accumulation appears as a three-step process. In the first step at low fluence there is no additional disorder observed. The second step is an effective fluence region where the disorder level increases almost proportionally with fluence. I found fluence rate dependence of the near-surface damage in this stage of damage accumulation. In the third step the disorder level tends to saturate and does not approach amorphization as the fluence increases. The saturation can be due to extremely dilute collision cascade formation in the near-surface region during He irradiation. Based on these results, I have chosen optimal measurement fluence and fluence rate for 3.5 MeV He BS/C analysis in SiC [4].

   b) I have determined the electronic stopping power for 3.5 MeV He ions along the <0001> crystallographic axis of 6H-SiC in standard BS/C measurement conditions. I appointed that using 20 % lower (average) electronic stopping power for the <0001> direction as compared to random direction an adequate energy-depth conversion in the evaluation of 3.5 MeV He BS/C spectra of the Si and C sublattices of SiC can be performed [8].

5. I applied the 3.5 MeV BS/C technique to measure the depth distribution of disorder in both the Si and C sublattices of 6H-SiC, irradiated with 200 keV Al ions to relatively low fluences along random direction at room temperature. All the implantation-induced relative disorder levels were below 0.2. Comparing the measured damage distributions to the results of SRIM computer simulations I have determined the effective displacement energies (E_d) as a function of the implantation fluence both for the Si and C sublattices. I found in the applied fluence range E_d varying between 14.8 eV and 19.3 eV for the carbon sublattice and between 24.8 eV and 26.8 eV for the silicon sublattice, respectively [5].

6. Using 3.5 MeV He BS/C technique, I have determined the depth distribution of disorder induced by 500 keV N implantation as a function of the fluence and the direction of irradiation with respect to the <0001> crystallographic axis of 6H-SiC.
   a) I have shown that the amount of damage can be significantly reduced by means of channeling implantation, especially at low fluences. I demonstrated that already a tilt angle of 4^{o} relative to the <0001> axis is equivalent to the random direction for implantation [6-8].

b) From BS/C spectrum analysis, profilometric measurements, computer simulations performed by the Crystal-TRIM code, and isochronal annealing experiments between room temperature and 800 °C I have concluded that the formation of disorder can be well described by the direct-impact, defect-stimulated amorphization model for SiC. The irradiation-induced disorder consists mainly of irradiation-induced point defects below a relative disorder level of about 0.2, whereas an amorphized fraction dominates damage build-up for higher disorder levels. The progress of disorder formation seems to depend only on the amount of nuclear energy deposited to Si and C target atoms for all of the applied initial orientations of the impinging N ions with respect to the crystallographic <0001> axis [8].

Utilization of the results

The results achieved by the use of electron paramagnetic resonance for the investigation of electron-irradiated SiC already led to a better understanding of formation and interaction of point defects. The findings are exploited in the control of processing of ion-implanted high power SiC diode and transistor structures.

The results obtained from the ion beam analytical study of ion implanted and annealed SiC are directly used in the tailoring of depth distribution of dopants and ion irradiation induced damage in SiC substrates in device processing.

The above research is conducted in collaboration with the Fraunhofer Institute for Integrated Systems and Devices FhG IISB, Erlangen.

Publications

This Ph.D. work is based on the following publications:

[1] **Z. Zolnai**, N.T. Son, C. Hallin, and E. Janzén: Annealing behaviour of the carbon vacancy in electron-irradiated 4H-SiC, Journal of Applied Physics 96 (2004) p. 2406

[2] **Z. Zolnai**, N. T. Son, B. Magnusson, C. Hallin, and E. Janzén: Annealing behaviour of vacancy- and antisite-related defects in electron-irradiated 4H-SiC, Materials Science Forum 457-460 (2004) p. 473

[3] N.T. Son, **Z. Zolnai**, and E. Janzén: Silicon vacancy related T_{V2a} center in 4H-SiC, Physical Review B 68 (2003) p. 205211

[4] N.Q.Khánh, **Z. Zolnai**, T. Lohner, L. Tóth, L. Dobos and J. Gyulai: He ion Beam Density Effect on Damage Induced in SiC During Rutherford Backscattering Measurement, Nuclear Instruments and Methods in Physics Research, B 161-163 (2000) p. 424

[5] **Z. Zolnai,** N.Q. Khánh, E. Szilágyi, E. Kótai, A. Ster, M. Posselt, T. Lohner, and J. Gyulai: Investigation of Ion Implantation Induced Damage in the Carbon and Silicon Sublattices of 6H-SiC, Diamond and Related Materials 11 (2002) p. 1239

[6] **Z. Zolnai,** N.Q. Khánh, T. Lohner, A. Ster, E. Kótai, I. Vickridge, and J. Gyulai: Damage Distributions Induced by Channeling Implantation of Nitrogen into 6H Silicon Carbide, Materials Science Forum 433-436 (2003) p. 645

[7] **Z. Zolnai,** A. Ster, N.Q. Khánh, E. Kótai, M. Posselt, G. Battistig, T. Lohner, and J. Gyulai: Ion Beam Analysis and Computer Simulation of Damage Accumulation in Nitrogen Implanted 6H-SiC: Effects of Channeling, Materials Science Forum 483-485 (2005) p. 637

[8] **Z. Zolnai,** A. Ster, N.Q. Khánh, E. Kótai, M. Posselt, G. Battistig, T. Lohner, and J. Gyulai: Influence of crystallographic orientation and Ion Fluence on Damage Accumulation in Nitrogen Implanted 6H-SiC, manuscript for Journal of Applied Physics

Further publications:

Journal papers:

[9] T. Lohner, N.Q. Khánh, **Zs. Zolnai**: Spectroellipsometric Characterization of Ion Implanted Semiconductors and Ellipsometry, acta physica slovaca, 48 (1998) p. 441

[10] E. Szilágyi, N.Q. Khánh, Z.E. Horváth, T. Lohner, G. Battistig, **Z. Zolnai**, E. Kótai and J. Gyulai: Ion Bombardment Induced Damage in Silicon Carbide Studied by Ion Beam Analytical Methods, Materials Science Forum 353-356 (2001) p. 271

[11] P. Petrik, N. Q. Khánh, Z. E. Horváth, **Z. Zolnai**, I. Bársony, T. Lohner, M. Fried, J. Gyulai, C. Schmidt, C. Schneider and H. Ryssel: Characterization of $Ba_xSr_{1-x}TiO_3$ films using spectroscopic ellipsometry, Rutherford backscattering spectrometry and X-ray diffraction, Journal of Non-Crystalline Solids, 303 (2002) p. 179

[12] P. Petrik, N.Q. Khánh, Z.E. Horváth, **Z. Zolnai**, I. Bársony, T. Lohner, M.Fried, J. Gyulai, C. Schmidt, C. Schneider, H. Ryssel: Non-Destructive Characterization of $SrBi_2Ta_2O_9$ films, E-MRS Spring Meeting 2002, June 18-21, 2002, Strasbourg, France, Materials Science in Semiconductor Processing 5 (2002) p. 141

[13] J. Balogh , I. Vincze, D. Kaptás, T. Kemény, T. Pusztai, L. F. Kiss, E. Szilágyi, **Z. Zolnai**, I. Kézsmárki, A. Halbritter, G. Mihály: Interface Magnetoresistance of Fe/Ag Multilayers, physica status solidi (a), 189 (2002) p. 621

[14] D. Gogova, H. Larsson, R. Yakimova, **Z. Zolnai**, I. Ivanov, B. Monemar: Fast growth of high quality GaN, physica status solidi (a), 200 (2003) p. 13

[15] N.T. Son, B. Magnusson, **Z. Zolnai**, A. Ellison, and E. Janzén: Defects in semi-insulating SiC substrates, Materials Science Forum 433-436 (2003) p. 45

[16] E. Janzén, I. G. Ivanov, N. T. Son, B. Magnusson, **Z. Zolnai**, A. Henry, J. P. Bergman, L. Storasta and F. Carlsson: Defects in SiC, Physica B 334-342 (2003) p. 15

[17] N.T. Son, B. Magnusson, **Z. Zolnai**, A. Ellison, and E. Janzén: Defects in high-purity semi-insulating SiC, Materials Science Forum 457-460 (2004) p. 37

Conference papers:

[18] **Zolnai Zsolt**: Az MFA kutatási területei: Implantált SiC minták vizsgálata ionsugaras analízissel. Talk at the ”Tavaszi szél 2000” meeting for young scientists and Ph.D. students (Apr 15, 2000, Szent István University, Gödöllő, Hungary), and in Abstract Book of the Conference

[19] **Z. Zolnai**, N.Q. Khánh, E. Szilágyi, Z.E. Horváth, and T. Lohner: Native Oxide and Ion Implantation Damaged Layers on Silicon Carbide Studied by Ion Beam Analysis and Ellipsometry, Proc. " XV International Conference for Physics Students ICPS 2000" (Aug 4-11, 2000, Zadar, Croatia), http://fizika.org/icps2000/sci/proc.html

[20] M. Serényi, Á. Nemcsics, J. Betko, **Zs. Zolnai**, N. Q. Khánh, Zs. J. Horváth: Sputtered a-SiGe:H layers for solar cell purposes, Workshop on Solid State Surfaces and Interfaces II, SSSI-II, (2000 June 20-22, Bratislava, Slovakia) Book of Extended Abstracts p. 65

[21] E. Szilágyi, E. Kótai, N.Q. Khánh, **Z. Zolnai**, G. Battistig, T.Lohner and J. Gyulai: Ion Implantation Induced Damage in Silicon Carbide Studied by Non-Rutherford Elastic Backscattering, Proc. 13th International Conference on Ion Implantation Technology, (Sept 17-22, 2000, Alpbach, Austria), IEEE (2001) p. 131

[22] N.T. Son, B. Magnusson, **Z. Zolnai**, A. Ellison, and E. Janzén: Magnetic resonance of large-area semi-insulating SiC substrates, Proc. of the American Physical Society Meeting (Austin, Texas, USA; March 3-7, 2003) Bulletin of The American Physical Society Meeting **48** (2003) p. 1322

[23] Zs. J.Horváth, M. Serényi, M. Ádám, B. Pődör, V. Rakovics, P. Turmezei, **Z. Zolnai**, I. Szabó, N. Q. Khánh: Vertical electrical transport in sputtered Al/a-SiGe/c-Si structures, 10th Joint Vacuum Conference, Sept. 28–Oct. 2, 2004, Portoroz, Slovenia, Program and Book of Abstracts p. 123

[24] Zs. J.Horváth, M. Serényi, M. Ádám, I. Szabó, V. Rakovics, P. Turmezei, **Z. Zolnai**, N. Q. Khánh: Electrical behaviour of sputtered Al/SiGe/Si structures, Solid State Surfaces and Interfaces IV, Nov. 8–11, 2004. Smolenice, Slovakia, Abstract Book p.16

Number of independent citations

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References

Åberg, D., A. Hallén, P. Pellegrino, and B. G. Svensson, Applied Physics Letters 78 (2001) 2908.

Gerstmann, U., E. Rauls, Th. Frauenheim, and H. Overhof, Physical Review B 67 (2003) 205202.

Harris, G. L., ed., *Properties of Silicon Carbide*, EMIS Datareviews Series No. 13, 1995

Jiang, W., C. M. Wang, W. J. Weber, M. H. Engelhard, and L. V. Saraf, Journal of Applied Physics 95 (2004) 4687.

Zetterling, C.-M., ed., *Process Technology for Silicon Carbide Devices*, EMIS Processing Series No. 2, 2002