Modelling of Point and Extended Defects in Group IV Semiconductors

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Submitted by Naomi Fujita, to the University of Exeter as a thesis for the degree of Doctor of Philosophy in Physics, September 2009.

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I certify that all material in this thesis which is not my own work has been identified and that no material has previously been submitted and approved for the award of a degree by this or any other University.

— Naomi Fujita
Abstract

In this thesis first-principles calculations of point and extended defects in diamond and silicon are reported. In single crystal diamond grown by chemical vapour deposition (CVD) dislocations are observed as mixed-type $45^\circ$ and edge-type dislocations lying along $(100)$ with $\frac{1}{2}(110)$ Burgers vectors. Results are presented on the core structures, core energies and electrical properties of both types of dislocations and their interaction with nitrogen is investigated. Then the focus turns to the brown diamond problem. Despite concerted research efforts, the origin of the brown colouration of diamond is still under discussion. Recently, the attention was drawn to vacancy-related defects. Experiments on type IIa diamonds indicate that the brown colour is caused by vacancy-type extended defects, however the shape and size of these defects remained unclear. In this work, the structural, electrical and optical properties of large spherical vacancy clusters and thin vacancy disks are investigated by means of density functional theory and the calculations are compared with recent experimental measurements on brown diamond. High pressure high temperature treatment (HPHT) of brown type Ia diamonds above $2000^\circ$C results in the loss of the brown colour and the formation of nitrogen-vacancy defects. The generation of such defects requires a source of mobile vacancies during the annealing process. It is suggested that the vacancy cluster model described in this thesis can explain the observed annealing behaviour since the break-up of the clusters leads to a supersaturation of mobile vacancies which readily complex with substitutional nitrogen atoms present in the material. Therefore, the effect of HPHT treatment of brown type Ia diamond is investigated by studying the formation energies of common and rare defects and estimates of their equilibrium concentrations at different annealing stages are given. Finally, an open problem also involving nitrogen, but in a different group IV semiconductor is considered. In Czochralski-silicon, nitrogen-related shallow thermal donors are formed between $500$ and $750^\circ$C. Until now the exact chemical composition and atomic structure of these defects are not well established. Here, it is shown that NO and NO$_2$ belong to the family of nitrogen-oxygen related shallow thermal donors. Based on the law of mass action the equilibrium defect concentrations are predicted. Finally, the theoretical results are compared to recent Fourier transform infrared (FTIR) spectroscopy measurements.
List of Publications

Peer-reviewed articles

- **Large spherical vacancy clusters in diamond – origin of the brown colouration?**  
  **N. Fujita**, R. Jones, S. Öberg, and P. R. Briddon  
  Diamond and Related Materials **18**, 843-845 (2009)

- **Theoretical investigation on the interaction of nitrogen with dislocations in single crystal CVD diamond**  
  **N. Fujita**, R. Jones, S. Öberg, and P. R. Briddon  

- **Nitrogen related shallow thermal donors in silicon**  
  **N. Fujita**, R. Jones, S. Öberg, and P. R. Briddon  

- **First-principles study on the local vibrational modes of nitrogen-oxygen defects in silicon**  
  **N. Fujita**, R. Jones, S. Öberg, and P. R. Briddon  

- **Electrical and optical properties of multivacancy centres in diamond**  
  R. Jones, L. S. Hounsome, **N. Fujita**, S. Öberg, P. R. Briddon  
  physica status solidi (a) **204**(9), 3059-3064 (2007)

- **Core reconstructions of the (100) edge dislocation in single crystal CVD diamond**  
  **N. Fujita**, A. T. Blumenau, R. Jones, S. Öberg, P. R. Briddon  
  physica status solidi (a) **204**(7), 2211-2215 (2007)

- **Local vibrational modes of N$_2$-O$_n$ defects in Cz-Silicon**  
  **N. Fujita**, R. Jones, S. Öberg, P. R. Briddon  

- **Theoretical studies on (100) dislocations in single crystal CVD diamond**  
  **N. Fujita**, A. T. Blumenau, R. Jones, S. Öberg, P. R. Briddon  
  physica status solidi (a) **203**(12), 3070-3075 (2006)
Conference proceedings

- *A Theoretical Study of Copper Contaminated Dislocations in Silicon*
  
  **N. Fujita**, R. Jones, S. Öberg, P. R. Briddon, A. T. Blumenau
  

- *Theoretical Aspects on the Formation of the Tri-interstitial Nitrogen Defect in Silicon*
  
  **N. Fujita**, R. Jones, T. A. G. Eberlein, S. Öberg, P. R. Briddon
  

- *Atomistic modelling of nitrogen related defects in silicon*
  
  **N. Fujita**, R. Jones
  

- *First-principle Study on the Identification of Nitrogen-oxygen defect complexes in Silicon*
  
  **N. Fujita**, R. Jones, S. Öberg, and P. R. Briddon
  

Presentations at international conferences

- *Properties of extended vacancy-type defects in diamond*
  
  DIAMOND 2008, 19th European conference on diamond, diamond-like materials, carbon nanotubes and nitrides, Sitges, Spain (oral presentation)

- *Properties of large spherical vacancy clusters in diamond*
  

- *Atomistic modelling of nitrogen related defects in silicon*
  
  5th Forum on the Science and Technology of Silicon Materials, Niigata, Japan (oral presentation, invited)

- *Identification of nitrogen related shallow thermal donors in silicon*
  
  12th GADEST conference 2007, Erice, Italy (oral presentation, Young Researcher Best Presentation Award)

- *Theoretical study of copper contaminated dislocations in silicon*
  
  12th GADEST conference 2007, Erice, Italy (poster presentation)
• **Theoretical study of gold trapped at dislocations in silicon**  
  24th ICDS conference 2007, Albuquerque/NM, USA (poster presentation)

• **Theoretical study of nitrogen related defects in silicon**  
  24th ICDS conference 2007, Albuquerque/NM, USA (poster presentation)

• **First principles calculations of the annealing stages in HPHT treatment of brown type Ia diamonds**  
  58th De Beers Diamond conference 2007, Warwick, U.K. (oral presentation)

• **Identification of nitrogen-oxygen defects in Cz-Silicon**  
  ECS fall meeting 2006, Cancun, Mexico (oral presentation)

• **Ab initio study of gold trapped at dislocations in silicon**  
  13th EDS conference 2006, Halle, Germany (oral presentation)

• **New structures of \(\langle 100\rangle\) dislocations in single crystal CVD diamond**  
  13th EDS conference 2006, Halle, Germany (oral presentation)

• **Theoretical studies on \(\langle 100\rangle\) dislocations in single crystal CVD diamond**  
  SBDD XI 2006, Hasselt, Belgium (oral presentation)
Acknowledgements

First, I would like to thank the School of Physics, the British Engineering and Physical Research Council (EPSRC) and the Diamond Trading Company (DTC) for providing resources and funding for the duration of my PhD at Exeter University.

I owe my deepest gratitude to my supervisor Bob Jones for giving me the opportunity to work in his group and for the guidance and continuous support he provided. He encouraged my involvement in various interesting projects over the years and gave me the chance to present our work at many exciting conferences throughout the world, which I greatly appreciate. In this context I would also like to acknowledge additional financial support that has been provided by the Institute of Physics (IoP) Semiconductor Physics Group, the Electrochemical Society’s (ECS) Electronics & Photonics Division (EPD) and the organising committee of the Silicon Materials Science and Technology Forum (Japan). Many thanks to all members of our local AIMPRO group (James, Thomas, Steve, Luke, Ines and Colin) for their companionship and to the many AIMPRO members outside Exeter, in particular Patrick Briddon (Newcastle) for his excellent code development and Sven Öberg (Luleå) for providing computational resources, but especially for his friendship and hospitality during my two very enjoyable and fruitful stays in Lapland – I doubt this thesis would be in its current state without the spontaneous invitation to Luleå I received this summer! Furthermore, I am grateful to Ben Hourahine (Strathclyde) and Alexander Blumenau (now at Wacker-Schott) for their help during the course of my PhD and for the careful proof-reading of parts of this thesis.

Further, I would like to acknowledge the fruitful discussions which I have had with people from the experimental world, amongst them, Philip Martineau, David Fisher, Riz Khan (DTC), Uschi Bangert, Rachel Barnes and Iain Godfrey (Manchester), Bert Willems (Antwerp), Jussi-Matti Mäki (Helsinki), Andrew Lang (Bristol), Gudrun Kissinger (IHP), Naohisa Inoue (Osaka) and Ole Anderson (Topsil).

Since I had the brilliant idea to start a new job before finishing my PhD, I must express my gratitude to my colleagues at work not only for their encouragement, but also for taking over some of my work during my absence. My employer is thanked for granting vacation leave and compensatory time off over the last few months. It was an immense challenge to accommodate both my job and my thesis, but now it’s done!!!

Finally, I would like to thank all my friends in Exeter and abroad for the various contributions they made to the non-scientific part of my life and, last but not least, my family for their ongoing support and sympathy.
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