Density Functional Theory Modelling of Intrinsic and Dopant-Related Defects in Ge and Si

Submited by Colin Janke to the University of Exeter as a thesis for the degree of Doctor of Philosophy in Physics.

December, 2008

Abstract

This thesis covers the application of the local density approximation of density functional theory to a variety of related processes in germanium and silicon. Effort has been made to use calculated results to explain experimentally observed phenomena.

The behaviour of vacancies and vacancy clusters in germanium has been studied as these are the dominant intrinsic defects in the material. Particular attention was paid to the annealing mechanisms for the divacancy as a precursor to the growth of the larger clusters, for which the electrical properties and formation energies have been studied. Some preliminary work is also presented on the germanium self-interstitial structure and migration paths.

Attention was then turned to a selection of dopant-vacancy defects in both silicon and germanium. An effort was made to explain recent experimental observations in silicon through investigating a number of defects related to the arsenic E-centre. Following this, the properties of donor-vacancy clusters in germanium were studied, and comparison with the results calculated for silicon suggest a significant parallel between the behaviour of the defects and dopants in the two materials.

Finally, extensive work was performed on the diffusion of phosphorus and boron in germanium. Diffusion of both dopants was studied via interstitial and vacancy mediated paths as well as by a correlated exchange path not involving any intrinsic defects. The results obtained confirmed current theories of the mechanisms involved in the diffusion of the two defects, while also expanding the knowledge of other paths and giving Fermi level dependences for the energy and mechanism for diffusion of the two defects. Boron diffusion was found to exhibit strong Meyer-Neldel rule effects, which are used to explain the unusually high diffusivity prefactors and energy barriers calculated from experimental measurements for this dopant.

Acknowledgements

The research presented between these covers owes its existence to many people, and I would like to take this space to express my gratitude.

First and foremost, my supervisor of the past three years, Prof. Robert Jones, whose enthusiasm, insight and guidance have been a great benefit, and who has always had time for my questions and puzzles.

Secondly, my family, especially my parents, Susan and Eric Janke, who kindled my interest in science and the natural world so many years ago, and without whose support and encouragement this thesis would never have been completed.

Various members of the extended AIMPro group are due a mention here, too: Patrick R. Briddon for making the code available and working tirelessly to maintain and improve it, Alexandra Carvalho and Naomi Fujita for their friendship over the past three years, Steve Sque, Luke Hounsome and Thomas Eberlein for their patience and guidance with my interminable questions and mistakes, Sven Öberg for allowing us to use his computers and spending significant time and effort on getting my calculations running and José Coutinho for his guidance and encouragement, and for showing me that you don't *have* to wear a suit to a conference.

Derek W. Palmer, for many insightful discussions on the experimentalist's view of the field and invaluable time spent proof-reading this thesis.

The Engineering and Physical Sciences Research Council for the financial backing which has allowed me to perform this research and present it at several conferences.

Finally, to Mark Roberts-Mapp, my long suffering house mate for helping me remain connected to the real world (and several less real ones) outside the walls of the Physics Department, and to my many other friends, particularly those involved with Heart of Pargon for making sure I didn't forget that there is more to life than solid state physics.

List of Publications

First Author

1. *Supercell and cluster density functional calculations of the thermal stability of the divacancy in germanium*
   C. Janke, R. Jones, J. Coutinho, S. Öberg and P. R. Briddon, Mat. Sci in semicond. Proc. **9**, 484 (2006)

2. *Ab initio investigation of boron diffusion paths in germanium*
   C. Janke, R. Jones, S. Öberg and P. R. Briddon, J. Mater. Sci.: Mater. Electron. **18**, 775 (2006)

3. *Supercell and cluster density functional calculations of the thermal stability of the divacancy in germanium*
   C. Janke, R. Jones, S. Öberg and P. R. Briddon, Phys. Rev. B, **75**, 195208 (2007)

4. *Ab initio studies of arsenic and boron related defects in silicon mesa diodes*
   C. Janke, R. Jones, S. Öberg and P. R. Briddon, Appl. Phys. Lett **90**, 152103 (2007)

5. *Ab initio investigation of boron diffusion paths in germanium*
   C. Janke, R. Jones, S. Öberg and P. R. Briddon, Phys Rev B, **77**, 075208 (2008)

6. *Ab initio investigation of phosphorus diffusion paths in germanium*
   C. Janke, R. Jones, S. Öberg and P. R. Briddon, Phys Rev B, **77**, 195210 (2008)

7. *Ab initio investigation of phosphorus and boron diffusion in germanium*
   C. Janke, R. Jones, J. Coutinho, S. Öberg and P. R. Briddon, Mat. Sci. in Semicond. Proc., in press

Collaborative Work

1. *Early stage donor-vacancy clusters in germanium*
   J. Coutinho, V. J. B. Torres, S. Öberg, A. Carvalho, C. Janke, R. Jones and P. R. Briddon, J. Mater. Sci: Mater. Electron., **18**, 769 (2006)

2. *Strong compensation of n-type Ge via formation of donor-vacancy complexes*
   J. Coutinho, C. Janke, A. Carvalho, V. J. B. Torres, S. Öberg, R. Jones and P. R. Briddon, Phys. B, **401**, 179 (2007)

3. *Self-interstitial in germanium*
   A. Carvalho, R. Jones, C. Janke, J. P. Goss, P. R. Briddon, J. Coutinho, S. Öberg, Phys. Rev. Lett., **99**, 175502 (2007)

4. *Limits to n-type doping in Ge: Formation of donor-vacancy complexes*
   J. Coutinho, C. Janke, A. Carvalho, S. Öberg, V. J. B. Torres, R. Jones, P. R. Briddon, Defects and Diffusion Forum, **273**, 93 (2008)

5. *Primary defects in n-type irradiated germanium: a first-principles calculation*
   A. Carvalho, R. Jones, C. Janke, S. Öberg and P. R. Briddon, Sol. Stat. Phen., **131-133**, 253 (2008)

6. *First-principles study of the diffusion mechanisms of the self-interstitial in germanium*
   A. Carvalho, R. Jones, J. P. Goss, C. Janke, S. Öberg and P. R. Briddon, J. Phys.: Cond. Mat., **20**, 135220 (2008)

Contents

List of Figures

List of Tables