THESIS POINTS OF THE Ph.D. THESIS

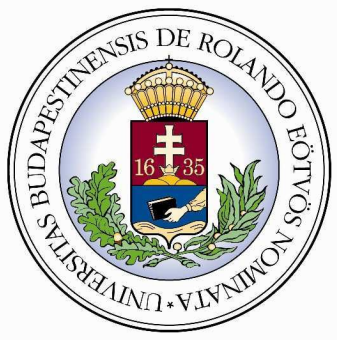
Identification of Point Defects in Semiconductors by Calculating the Hyperfine Tensor

Krisztián Szász
Physicist

Supervisor:
Dr. Ádám Gali
Scientific Advisor, Doctor of Science

Loránd Eötvös University Faculty of Science
PhD School of Physics
Material Science and Solis State Physics Programme

School Leader: Dr. László Palla
Programme Leader: Dr. János Lendvai



Wigner Research Centre for Physics of HAS, Institute for Solid State Physics and Optics
Budapest
2015

1. Introduction and Goals

The main component of the electronic equipments is the semiconductor material, which is mostly silicon. Although it is easy and cheap to construct excellent devices from this material, under extreme conditions, e.g. at high temperature, in radioactive radiation or for high power, high frequency electronics silicon is no longer suitable. Previously it was showed that the wide band gap semiconductors such as diamond, silicon carbide or gallium nitride are appropriate since they have better physical parameters (larger melting point, larger breakdown voltage) than that of silicon. However, these materials are not perfect crystals, they contain several point defects. It is important to study and know the microscopic behavior of these point defects because they may change the electrical, magnetic and optical properties of the semiconductor. The point defects have negative aspect, they can be traps for the charge carriers, thus they can prevent the appropriate operation of the devices. From another point of view, the point defects in semiconductors play an important role in the field of quantum information, quantum optics and spintronics, which have become hot topics. Namely, the point defects that have ground state with non zero spin (paramagnetic), the spin state of the point defect may be coherently manipulated by light even at room temperature. Therefore, these type of point defects are excellent candidates for realizing solid state quantum bit (qubit). Moreover, in some cases not only the spin state, but also the spin of the nuclei can be controlled, which is notable in the field of creating quantum memory and remote sensing. Other paramagnetic point defects can reduce the coherence time of a qubit or spin state of a nucleus. To avoid this loss of information it is also necessary to study the point defects. Noteworthy, some point defects are recently engineered to act as single photon source, which are needed to implement quantum key distribution and photonic quantum information processing. The study of point defects in semiconductors is one of the hot topics of today, new papers are being published daily in prestigious journals since the physical properties are not completely understood and the possibilities of the application are not yet fully utilized.

Based on the above mentioned motivations I calculated the hyperfine tensor of paramagnetic point defects in silicon carbide, silicon and diamond. The hyperfine interaction is closely related to the spin density at the nucleus and around the nucleus. By means of the spin density distribution stemming from the point defect, the structure of the defect can be described and the physical properties can be understood. The spin density can be mapped in the electron paramagnetic resonance (EPR) or in the electron nuclear double resonance (ENDOR) measurements by the interaction between the electron spin of the

defect and the spin of the nucleus. This interaction results in the hyperfine splitting of the observed lines. The analysis of this splitting reveals the distribution of the spin density. Comparing the calculated and the measured hyperfine tensors, the point defect can be identified. Besides the identification, the goal was to determine the hyperfine structure of the point defects accurately. This makes it possible to predict the hyperfine structure of a not yet studied system or to clarify the experimental contradictions for a given system. Moreover, the hyperfine interaction plays a key role in the manipulation of the nuclear spin and the loss of information. Thus the knowledge of the hyperfine tensor contributes to understanding these processes as well as helps to find new candidates for the realization of quantum information devices.

2. Methods

I calculated the hyperfine tensor and the spin density distribution within the framework of the Kohn-Sham density functional theory. For the calculations I utilized the VASP (Vienna Ab Initio Simulation Package) code. This code applies plane wave basis set and the all-electron projector augmented wave (PAW) method. With this method the spin density can be calculated close to the nuclei accurately. I executed the code in Hungarian and international supercomputer centers. For modeling the defects I used 400-500-atom supercells. The optimal geometry was found by the conjugate gradient method. The Brillouin-zone sampling was reduced to the Γ-point, however in some cases the $2\times2\times2$ Monkhorst-Pack-scheme was needed. For the approximation of the exchange-correlation term I employed the PBE and the HSE06 functionals.

3. Thesis Points

1. Considering well-known and promising point defects I showed that the most accurate results on the hyperfine tensor can be achieved by applying the hybrid HSE06 functional for the estimation of the exchange-correlation functional and add the contribution of core spin polarization to the Fermi-contact term. In contrast to previous expectations in some cases the contribution can be enormously large [1].

    a) For NV-centre I found that the using of the PBE functional, which needs less computational time, is also appropriate. In this case the core contribution should not be considered since the underestimation of the localization of the defect wave functions and the neglect of the spin polarization of the core electrons

compensate each other. Also, the HSE06 functional together with the contribution of the core spin polarization provides the accurate hyperfine tensor [1].

2. I calculated the hyperfine structure of the niobium atom in silicon vacancy (Nb_{Si}^{0}) and the niobium atom in the carbon-silicon divacancy (Nb_{Si}-V_{C}^{0}) in 4H-SiC. Comparing the calculated and the EPR-measured hyperfine values for the niobium and the adjacent silicon atoms, I concluded that the only observed niobium-related EPR-spectrum comes from the Nb_{Si}-V_{C}^{0}. Thereby, I verified the previous statement that the niobium forms an asymmetric split vacancy complex, thus this is the most stable niobium-related defect in SiC [2].

3. By the calculation of the hyperfine tensor I showed that the new EPR-spectra found on N-doped 4H-SiC samples irradiated by low-energy (250 keV) electrons is related to the negatively charged carbon vacancy at the quasi-cubic site ($V_C(k)^-$). Besides, I provided an explanation for why the symmetry of the hyperfine structure changes with increasing the temperature. Indeed, at low temperature ($\sim$30 K) the symmetry is C_{1h}, at high temperature ($\sim$100 K) it is C_{3v}. Moreover, two geometries were found with C_{1h} symmetry but with different hyperfine structures. In both geometries the C_{1h} symmetry can be formed in three ways, and the energy barrier between the states can be overcome thermally. At elevated temperature these three configurations are equally occupied, the spin density migrates among the three silicon atoms, which results in a C_{3v} symmetry [3].

    a) By means of the formerly determined charge transition levels I showed that the negative-U property of the h substitution is weaker than that of the k substitution, and the $(-|0)$ level lies deeper at h site than at k site. With these results I could explain the temperature dependence of the EPR-spectra. The calculated charge transition levels are in line with the experimental results, which further supports the identification based on the calculated hyperfine values [3].

4. In 3C-, 4H- and 6H-SiC nitrogen is very common impurity, which resides at the carbon site (N_C). I examined the hyperfine structure of the N donor in 3C-SiC at the k, in 4H- and 6H-SiC at the h or k sites. Based on the comparison of my calculation with previous and new experimental results obtained by our colleagues in Linköping I could clarify the contradictory hyperfine structure of the N donor. I found that in all of the SiC polytypes the spin density is localized mainly on carbon

atoms and between the interstitial channel of the silicon atoms. Moreover, I showed that for 3C-SiC weak hyperfine interaction occurs with the N donor and with some carbon atoms. For 4H-SiC the h and the k substitutions can be distinguished by the hyperfine values measured on the N donor or on the silicon atoms located around the N donor. Similarly, for 6H-SiC distinction can be made between the hexagonal and the quasi-cubic sites, as well, and even the two quasi-cubic sites, k_1 and k_2 can be separated because remarkable hyperfine value can be found on the silicon atom located along the c-axis only for the k_1 substitution [4].

5. I studied the neutral carbon-antisite vacancy pair (C_{Si}-V_C) in 4H-SiC. I showed that the system exhibits $S = 1$ high spin ground state with C_{1h} symmetry and not the expected $S = 0$ with C_{3v} symmetry. By means of the calculated hyperfine tensor, charge transition levels, zero field splitting and the excitation energies I pointed out that the spin state of the electron of this defect can be manipulated similarly to those of NV-centre in diamond. Moreover, the calculated hyperfine structure revealed that it is possible to create entanglement between the electron spin and the nuclear spin of the carbon or silicon, that is, the nuclear spin can also be controlled. The calculated hyperfine structure can be useful in the EPR measurements when the identification of the defects in 4H-SiC is needed [5].

4. Conclusions

The method for the calculation of the hyperfine tensor of point defects in semiconductors which was presented and applied in this thesis, is a very efficient tool for studying the point defects. Comparing the simulated hyperfine splitting with the measured EPR-spectrum, the microscopical origin of the spectrum can be found, and the defect can be identified. Beyond the identification, the electron spin-nuclear spin entanglement and the possibility of the polarization of the nuclear spin can be studied by knowing the hyperfine structure. In this case the weaker hyperfine interaction plays the key role, contrary to the case of identification.

Publications Related to the Thesis Points

[1] K. Szász, T. Hornos, M. Marsman, and A. Gali, *Physical Review B* **88**, 075202 (2013).

[2] N. T. Son, X. T. Trinh, A. Gallström, S. Leone, O. Kordina, E. Janzén, K. Szász, V. Ivády, and A. Gali, *Journal of Applied Physics* **112**, 083711 (2012).

[3] X. T. Trinh, K. Szász, T. Hornos, K. Kawahara, J. Suda, T. Kimoto, A. Gali, E. Janzén, and N. T. Son, *Physical Review B* **88**, 235209 (2013).

[4] K. Szász, X. T. Trinh, N. T. Son, E. Janzén, and A. Gali, *Journal of Applied Physics* **115**, 073705 (2014).

[5] K. Szász, V. Ivády, I. A. Abrikosov, E. Janzén, M. Bockstedte, and A. Gali, *Physical Review B* **91**, 121201(R) (2015).

Other Publicarions

[6] A. Szállás, K. Szász, X. T. Trinh, N. T. Son, E. Janzén, A. Gali, *Journal of Applied Physics* **116**, 113702 (2014).

[7] V. Ivády, R. Armiento, K. Szász, E. Janzén, A. Gali, I. A. Abrikosov, *Physical Review B* **90**, 035146 (2014).

[8] K. Szász, V. Ivády, E. Janzén, A. Gali, *Materials Science Forum* **778-780**, 499 (2014).

[9] X. T. Trinh, K. Szász, T. Hornos, K. Kawahara, J. Suda, T. Kimoto, A. Gali, E. Janzén, N. T. Son, *Materials Science Forum* **778-780**, 285 (2014).