Silicon Carbide 3C-SiC phase band structures calculation in DFT

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Abstract. The 3C-SiC Silicon Carbide phase doped by P, Ga, and N atoms was analyzed in the framework of Density Functional Theory. The physical parameters, changing with time due to N concentration increase, were calculated. Crucial statements about the existence of the deepest level were checked. Calculations of band structures were performed using the software applications VASP and Siesta. The plane wave basis was used in the first case and the orbital basis in the frame of the virtual crystal approach in the second one.

1. Introduction

The motivation for this work was research in the field of betavoltaics technology with C-14 [1, 2]. In particular, we are interested in using the C-14 isotope inside Silicon Carbide to generate electrical energy. We will consider the 3C-SiC silicon carbide phase that is obtained as a result of endotaxy. This structure works as a beta converter with a p-n junction. To create the p-n junction, heterostructure or Schottky diode, it is necessary to dope Silicon Carbide by Ga, P [1].

Irradiation of the structure with beta particles leads to both structural transformations and changes in physical parameters that can affect the efficiency of beta energy conversion. We discuss the band structure of a semiconductor and its band gap width.

Due to the development of numerical methods and the increasing computational power, approaches based on the Density Functional Theory (DFT) has become popular for studying of the materials atom structure [3,4]. It also allows one to investigate band structures.

These methods do not consider the interaction of radiation with matter, but elucidate impact of radiation on its structure. We are dealing with the radioisotope C-14, which decays into a nitrogen atom N through the following reaction,

\[ ^{14}\text{C} \rightarrow ^{14}\text{N} + e^- + \bar{\nu}_e, \]

having the half-life of 5730 years. The nitrogen concentration increases over time in the 3C-SiC structure.

Thus, in the simplest case, we have three types of doping atoms in the 3C-SiC structure: Ga, P, and N with changing over time a number of the last ones. N-doped structures have already been analysed in the paper [5] using ab initio calculations. According to these calculations, the doping does not lead to the appearance of new bands in the band structure, but it shift up the Fermi level.

It is known that the position of the Fermi level in the band structure of a conductor has the significant influence on its physical properties and determines the probability of filling the energy levels in the semiconductor with electrons. Under doping of a semiconductor as well as expose it by some radiation, defects occur which form some levels in the band structure with various depths. The Fermi level changes...
its position. This phenomenon is called pinning (or fixing) the Fermi level. It is universal for all semiconductors and does not depend on the irradiation conditions and the background of the material. This phenomenon was discussed in details in works [6–8], and in [9] the theoretical model for pinning the Fermi level when a semiconductor is irradiated by high-energy radiation was developed.

To study the betavoltaic effect in the silicon carbide containing a carbon radioisotope, it is important to know exactly how the Fermi level moves under doping and further decay, because this helps to describe semiconducting properties of the sample during experiments.

Continuous generation and recombination of electrons and holes associated with the electron emission caused by the radioisotope decay occur in the sample. This can lead to the appearance of localized states which are not impurity in nature. We consider these states as radiation defects and apply the model by Brudnyi described in [9] as a ‘correction’ to the position of the Fermi level in the structure of the semiconductor.

Thus, we aim to calculate the band structure of the 3C-SiC Silicon Carbide phase, monitoring the change in the Fermi level in dependence on doping, and verify Brudnyi’s claims.

2. Calculation methods and other details
We have chosen a structure for research with cell containing two atoms [10]. Atom doping was realized in two ways:

- substitution of atoms in the supercell $2 \times 2 \times 2$
- calculating the proportion of doping in the virtual crystal approach (VCA) [11]

For the first task we used SOD [12] to find nonequivalent positions of the dopant. Thus, a supercell of 16 atoms allows to insert one doped atom in one way. Two or three atoms can be inserted in 7 ways. Thus, we consider three cases of doping.

The calculation of supercells was performed using the Vienna Ab Initio Simulation Package (VASP) [13]. The recommended pseudopotentials and exchange-correlation functional of PBE were selected [14] in the generalized gradient approximation. A basic set of plane waves was used. The limit value of the kinetic energy of waves in the base set was selected at the level of 600 eV. The length of the partition of the reciprocal space is 15 Å.

VCA was performed in the framework of Siesta software [15] with orbital basis. In all Siesta simulations, cutoff parameter was 200 Ry and geometry relaxation was performed by the conjugate gradient method.

3. 3C-SiC band structure
The band structures of pure semiconductors have already been studied in ab initio calculations [16]. We reproduced this calculation in both VASP and Siesta software. The band structure is shown in the Figure 1(a).

Calculations using the DFT approach suggest that nitrogen doping does not lead to the appearance of new bands in the band structure of the semiconductor. However, it causes the Fermi level to shift up when the concentration of atoms increases. This is consistent with statements in [5], although the authors considered much smaller concentrations. In our calculation, for example, in the VCA approach, when doping is 6.25% (this corresponds to 1 atom-dopant in a supercell of 16 atoms), the Fermi energy is $-3.34$ eV. For a concentration of 12.5% (this corresponds to 2 atoms-dopants in a supercell of 16 atoms), the Fermi energy is $-2.77$ eV.

Band gap of Silicon Carbide with radiation defects is uniquely determines the Fermi level shift according Brudny’s statement. Our calculations give the increase in the Fermi level by 0.57 eV with increasing nitrogen concentration. We can compare these results to calculate the position of the deep level based on the experimental value of the band gap width of 2.36 eV for SiC (Figure 2).

The results of ab initio calculations and the analytical approach don’t converge numerically. The inflection point of the Green function is slightly lower than 0.5 eV. At the same time, the width of band
Figure 1. (a) Band diagram of silicon carbide 3C-SiC; (b) Binding energy (the energy of dissolution in this case) in eV

Figure 2. G(E) is the second derivative of the green function. The inflection point corresponds to a deep level. A(E) and F(E) are partial contributions from the valence band and conduction band.

gap in DFT calculations is always lower than the experimental value. It is necessary to check whether the doping atoms are defects in the crystal structure. This will be discussed in the next paragraph.
4. Nitrogen atom position inside the Silicon Carbide phase

The thermodynamic stability of selected phases was determined by the value of the binding energy per atom (convex hull method). The calculations were performed in the VASP program for supercells. The following formula was used for calculations:

\[ E_b = \frac{E - N E_{X_1} - M E_{X_2}}{N + M}, \] (1)

where \( E_{X_1} \), \( E_{X_2} \) – one atom energy of pure substance, \( E \) – energy of total structure, \( N \) and \( M \) – number of atoms respectively. Since doping atoms substitute Carbon atoms, it would be reasonably to expect negative values of binding energy. However, they are positive (Figure 1(b)).

This means that the new Nitrogen atom leaves the crystal structure after the decay of \(^{14}\)C. The phase is destroyed. Therefore, we can consider all doping atoms P, Ga, N as defects in the crystal structure.

5. Conclusion

We have reviewed the 3C-SiC phase in various DFT implementations and obtained agreement of the results of band structure calculations with the results of the work of the predecessors. Based on this, we calculated the position of the Fermi level in the VCA approach in the Siesta package. This allowed us to compare our results with the Brudnyi model of the deep-level position. Also, we were able to verify in the calculations in the VASP package with supercells that the doping atoms are not part of the structure and, indeed, can be considered as defects.

Returning to the deep-level problem, we can say that the Brudnyi model should accord our calculations. Inconsistencies between the model and the calculations may indicate either an imperfection of the numerical methods, or necessity to specify in more details which kinds of defects are consistent with the Brudnyi model.

Acknowledgments

Authors are grateful to organizers of the VI international conference Laser, plasma research and technology-LaPlas 2020 in MEPhI for their reception, discussions and suggestions.

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