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Electronic properties of SiC polytypes: Charge neutrality level and interfacial barrier heights

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ABSTRACT

The position of the intrinsic charge neutrality level (CNL) in a number of silicon carbide polytypes has been determined based on the calculations within density functional theory and quasiparticle G_0W_0 approximation. We have considered eight polytype structures of SiC, including the simplest cubic one as well as various hexagonal and rhombohedral polymorphs. The theoretical band gaps calculated within G_0W_0 are in excellent agreement with experiment. The CNL energy positions in SiC polytypes are found to be very close to each other with average value of 1.76 eV above the valence band maximum. On the basis of the performed CNL computations, the electronic properties of irradiated silicon carbide and the energy diagrams of the metal/SiC interfaces and some heteropolytype junctions based on SiC have been analyzed. We also give estimations of the electron affinity in SiC polytypes as a function of their hexagonality.

1. Introduction

Silicon carbide forms a large variety of polytypes with the same chemical composition, including the cubic polytype 3C-SiC with the sphalerite lattice, the hexagonal nH-SiC polytypes and the group of rhombohedral nR-SiC crystals [1,2]. These materials exhibit close total energies (per formula unit), parameters of the chemical bonds, thermal and mechanical properties. The outstanding electronic, thermal and chemical characteristics of SiC enable wide applications in high-power and harsh-environment electronic devices [1,3]. Silicon carbide also attracts attention as a promising material for the production of nuclear radiation detectors due to its low density and a high threshold energy for the formation of radiation defects. The effect of irradiation with high-energy particles on the properties of SiC has been investigated in a large number of works [4–6]. These studies have shown that the treatment of SiC polytypes with various types of high-energy radiation leads to an increase in the electrical resistance of both *n*- and *p*-type samples and moves the Fermi level deep into the forbidden band. However, the wide band gap in silicon carbides ($E_g = 2.4–3.3$ eV) makes it difficult to experimentally ascertain the actual limiting values of the resistivity and accordingly the limiting position of the Fermi level (F_{lim}) in the irradiated crystals from the direct Hall effect or thermal emf measurements. Meanwhile, it is known that the position of F_{lim} in the irradiated material is identical to the branch point of the complex band structure, which in the literature has been associated with the level of local charge neutrality (CNL) [7,8]. The location of CNL relative to the band gap edges corresponds to the energy where the character of the gap states changes from the predominantly valence-band-like to the conduction-band-like. The principle of

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local charge neutrality has proven its relevance for understanding many problems in semiconductor physics. CNL defines not only the bulk electronic properties of a defective crystal, but also the properties of its surface. In addition, it specifies the heights of the Schottky barriers and band discontinuities in the semiconductor heterojunctions [8,9]. Therefore, the knowledge of CNL position in a given compound allows one to predict the influence of high irradiation doses on the electronic characteristics of a material, and to describe the energetic parameters of the interphase boundary.

The previous studies of CNL in silicon carbide are incomplete and have been done mainly for the simplest polymorphs. The present work is aimed at calculating the CNL energy position in several hexagonal and rhombohedral SiC polytypes, in addition to the cubic polytype. The obtained theoretical data are then used for analysis of the electronic properties of a bulk SiC saturated with intrinsic lattice defects, and for investigation of metal/SiC contacts and some SiC^a/SiC^b heteropolytype interfaces.

2. Calculation methods

The calculations of CNL were carried out on the basis of three analytical models – as the dielectric mid-gap energy ($CNL_1 = \langle E_g \rangle/2$), as the intrinsic local chemical potential (CNL_2) [7] and as the deepest gap state (CNL_3) of a semiconductor [8]. These models have been successfully applied earlier for assessing the CNL position in Si, C (diamond), 3C-SiC, and a number of A^3B^5 [7,8,10–12] and A^3B^6 [13] compounds. The methods are well described in the referenced papers; therefore, we will not discuss them here.

Determination of CNL requires energies of the valence bands and a sufficiently large number of the conduction bands. At present, for estimations of CNL in different crystals the first-principles band structures are employed, which are usually calculated within the framework of the density functional theory (DFT) using the local (LDA) and the various forms of semilocal (GGA) approximations for the exchange-correlation potential [10–13]. However, a well-known underestimation of the conduction band energies within DFT introduces significant errors in such computations. This is a major shortcoming of DFT in semiconductor modeling, which does not allow one to directly rely on the results of calculations for unoccupied states and requires further correction of the data obtained. A simple and widely used way to overcome this problem consists in application of the so-called scissor operator which moves all the conduction bands upward in energy so as to enlarge the DFT band gap to the measured value. In the present work we employed a theoretically more consistent approach to determine the band gap energies from the quasiparticle calculations in the G_0W_0 approximation.

Our electronic structure calculations within the DFT-LDA and G_0W_0 computational schemes were carried out with Abinit code [14] using the plane-wave basis set and norm-conserving pseudopotentials of Troullier-Martins type. The plane-wave energy cutoff was set to 653 eV (48 Ry), and the convergence criterion was set to 10^{-5} eV during the electronic iterations. The Brillouin zone was sampled by Monkhorst-Pack meshes with sizes of $4 \times 4 \times 4$ (3C-SiC), $6 \times 6 \times 4$ (2H-SiC), $6 \times 6 \times 2$ (4H-SiC, 6H-SiC) and $6 \times 6 \times 1$ for the other polytypes. The energy band computations were performed for crystal structures with optimized atomic positions. The structure optimization was carried out at the fixed lattice parameters a and c, which were taken from the X-ray diffraction measurements. Note that in the case of 9R-SiC and 10H-SiC polytypes the experimental data are not available, so here we carried out a full optimization of the lattice constants and atomic positions using the PBEsol functional, which yields structural parameters of covalent-ionic compounds close to the experiment [15,16].

3. Results and discussion

3.1. CNL and properties of a defective SiC

The calculated values of E_g and the positions of CNL relative to the top of the valence band are presented in Table 1. The comparison of the G_0W_0 band gaps with the results of measurements [2], performed at a temperature of up to 4 K, shows excellent agreement. Our results also allow us to estimate for the first time the E_g values for 10H- and 9R-SiC structures where the experimental data are not available.

Table 1 shows how the E_g varies with change in the degree of SiC hexagonality $D = n_h/(n_c + n_h)$, where n_c and n_h are the numbers of cubic and hexagonal lattice sites occupied by atoms. The hexagonality of a polytype may vary from zero (3C-SiC)

Table 1
The band gap E_g from quasiparticle calculations within the G_0W_0 approximation, the CNL energy positions from three analytical models ($CNL_{1\text{-}3}$) and their averaged values $\langle CNL \rangle$ (with respect to the valence band top, in eV). The asterisk marks E_g from the exciton measurements (T = 2–4 K).

Polytype	Zhdanov notation	Hexagonality D, %	E_g, calc.	E_g, expt. [2]	CNL_1	CNL_2	CNL_3	$\langle CNL \rangle$
3C-SiC	∞	0	2.38	2.42, 2.39*	1.86	1.64	1.73	1.74
2H-SiC	11	100	3.33	3.33*	1.76	1.65	1.87	1.76
4H-SiC	22	50	3.26	3.28, 3.26*	1.85	1.71	1.88	1.81
6H-SiC	33	33.3	3.05	3.02	1.81	1.70	1.84	1.78
8H-SiC	44	25	2.77	2.80*	1.78	1.68	1.79	1.75
10H-SiC	55	20	2.67		1.78	1.66	1.74	1.73
	3322	40	3.00		1.80	1.68	1.81	1.76
9R-SiC	$(12)_3$	66.7	3.25		1.81	1.66	1.83	1.77