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Induced defect levels of P and Al vacancy-complexes in 4 *H*-SiC: A hybrid functional study

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ABSTRACT

The electronic behaviour of high-dose phosphorus implanted in 4 *H*-SiC is mainly desirable to obtained lower sheet resistance of 4 *H*-SiC. Al doping on the other hand acts as an acceptor, improves the dielectric properties of 4 *H*-SiC and has very low diffusivity in SiC. Using a hybrid density functional theory, we investigated the properties of Al and P defect-complexes in 4 *H*-SiC a wide band-gap semiconductor that is promising for applications in high-frequency and high-temperature electronic device. We show that vacancy-complexes formed by P_{Si} and Al_{Si} are more energetically stable than those formed by P_C and Al_C. The defects with silicon vacancy are predicted to experience more lattice distortion compared to those formed with carbon vacancy. While vacancy-complexes formed with P_{Si} or P_C and V_C induced double donor levels, vacancy-complex formed with substitution of P and V_{Si} induced negative-U charge state ordering. The Al with V_C related vacancy-complexes induced deep single donor and acceptor levels, and Al with V_{Si} induced only acceptor and negative-U ordering.

1. Introduction

One of the most promising wide band gap semiconductors is SiC. This is owing to the fact that its well known polytypes (2*C*, 3*C*, 4 *H*, 6 *H*) have significant application in extremely severe harsh environments (high-temperature, high-frequency, and high-power electronic devices). The 4 *H*-SiC amongst the commercially available SiC polytypes is more promising for application in metal-oxide-semiconductor field-effect-transistors (MOSFETs) high-power electronic devices. This is as a result of 4 *H*-SiC having a relatively high bulk electron mobility and small anisotropy compared to other well known polytopes [1]. The application of 4 *H*-SiC for high-power electronic device is not free from defects activities. Defects are known to influence the performance of wide or narrow band gap semiconductor materials including 4 *H*-SiC. Defects that enhances the performance of a device are desirable and should intentionally introduced [2–4]. Several experimental [[5–17] and theoretical [18–22] (most especially using the well known density functional theory) studies of point defects in 4 *H*-SiC have been reported. Point defects such as substitution, interstitials, vacancy and defect-complexes (interstitial-complex, vacancy-complex or antisite) have been reported in literature [18,19,23–26]. Report on the nuclear transmutation proceeding under high energy doping of Si and SiC by P suggests that an *n*-type phosphorus doped layer induced radiation damage defects in SiC [27]. To realized a high-performance SiC electronic device, electronic behaviour of high-dose phosphorus-ion implanted 4 *H*-SiC was reported by Negoro et al. [28]. The researchers suggest that in order to reduce the resistivity of Ohmic contacts as well as source and drain regions in field-effect transistors (FET), ion implantation with a high donor dose into SiC is required. As a result, N or P implantation is commonly used for this purpose. P implantation has been used to obtained lower sheet resistance in 4 *H*-SiC [29]. Recently, Okamoto et al. [30] have shown that an improved channel mobility of 4 *H*-SiC MOSFETs on Si face through P doped gate oxide is attainable. SiC is the only known wide band gap material that grows a thermal oxide (SiO_2), which makes it well suitable for the fabrication of MOSFETs [31]. This possibility comes with some challenges of deteriorating high density of interface at SiO_2/4 *H*-SiC. However, studies have shown that the interface state density can be decreased by over oxidation of P implanted in 4 *H*-SiC substrates [1,30,32]. Phosphorus implanted into 6 *H*-SiC shows ionisation energies of 80 and 110 meV for the hexagonal and cubic lattice sites, respectively. These ionisation energies are almost equivalent to those observed for nitrogen [17]. Whereas as reported in Ref. [33], where low sheet resistance is required in a device, it is advantageous to replace N with P. This is based on the fact that with comparable doping, thermal processing under equilibrium conditions, sheet resistances of P-implanted in 4 *H*-SiC are in an

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order of magnitude lower than those measured in N-implanted in 4 H-SiC [34]. While the ionisation energies of P implanted in 4 H-SiC is about 0.10 eV higher than those of N-implanted, the carrier concentration of the former is about a factor of five lower than the latter when subjected under annealed temperature of 3000 °C. Although not with the expense of higher mobility for the P-implanted in 4 H-SiC which does not offset the lower concentration and making the resistivity of P-implanted in 4 H-SiC to be higher than those of the N-implanted in 4 H-SiC. While for low dose application, one will consider the N-implanted to be energetically favourable, but on the contrary for high dose application and sheet reduction, P implanted in 4 H-SiC is desired [35]. During the implantation of P in 4 H-SiC, it is expected to caused crystal damage and introduced new defects which could enhance the performance or on the worse case scenario, act as a recombination centre therefore decreasing the operational power of the device. Despite the fact that small scale production of SiC power FET and Schottky barrier have started, there are varieties of point and extended defects still present in SiC epitaxial wafers [36]. Bockstedte et al. [37] have previously reported abundance of P and N related defects using an ab initio method. The researchers shown that the calculation of formation energies give access to the electrically active defects. According to Ref. [37], complexes with vacancy, antisite and interstitial are suggested to be stable. Furthermore, Bockstedte et al. [37] suggests that the phosphorus-vacancy complexes activation is only limited by the onset of precipitation. Al, a p-type dopant in 4 H-SiC has a low diffusivity and a high solubility [38]. But a well know basic physical problem is the low ionisation rate of p-type impurity atoms. For example, experimental results on donor-acceptor pair luminescence show that the ionisation of $\mathrm{Al_{Si}}$ lies within the value of 0.20–0.19 eV [39]. Al is mainly introduced in 4 H-SiC via ion implantation. Al related defect-complexes in 4 H-SiC has been reported, where it was established that aluminium can form thermally stable complexes with carbon interstitial ($\mathrm{C_i}$) and carbon vacancy ($\mathrm{V_C}$) inducing deep levels in the band gap [40,41]. Al defect-complex is suggested as a possible reason for the imperfect activation rate of a shallow aluminium acceptor in the damaged region of Al-implanted in SiC. Despite the fact that several studies on defects in 4 H-SiC have been theoretically [37,40,41] reported (for interstitial, vacancy, substitution, interstitial-complexes, vacancy-complexes or antisites), there are more that need to be investigated either experimentally or theoretically. For example complexes formed with N and either C or Si vacancy or interstitial have been reported, but detail reports on P or Al complexes formed with either $\mathrm{V_C}$ or $\mathrm{V_{Si}}$ are lacking and hence the motivation of this study.

In this report, we have used the Heyd, Scuseria and Ernzerhof (HSE06) [42] hybrid functional within the framework of the density functional theory (DFT) to model the electronic and total energies of P or Al related vacancy-complexes in 4 H-SiC. The formation energy and binding energies as well as the thermodynamic charge state transition energies were calculated. While our results reveal that the vacancy-complexes with a carbon vacancy induced both donor and acceptor levels, the vacancy-complexes with silicon vacancy exhibit the properties of negative-U ordering in the band gap of 4 H-SiC. The complexes with a silicon vacancy experienced more lattice distortion compared to those formed with a carbon vacancy.

2. Computational details

DFT based on the generalized Kohn-Sham theory method as implemented within the Vienna *Ab-initio* Simulation Package (VASP) [43,44] was used to perform all first principle calculations. the projector-augmented wave (PAW) method [43,45] was used to describe the valence electrons, and the exchange-correlation functional was approximated using the HSE06 hybrid functional with generalized gradient approximation (GGA) functional of Perdew, Burke, and Ernzerhof (PBE) [46]. The HSE06 functional provides partial cancellation of self-interaction and has been used to predict accurate structural, energetics and band structures of semiconductor materials [47,48]. This is in contrast to the local density approximation (LDA) or the GGA which severely underestimate band gap of materials and thereby wrongly predicting the electrically active induced defect levels in the band gap [20,49–51]. For the HSE06, a default mixing parameter of 25% and 0.2 $\mathrm{Å^{-1}}$ screening parameter was used for all calculations. It is sufficient to say that the 25% fraction of exact Hartree-Fock exchange and 0.2 $\mathrm{Å^{-1}}$ screening parameter were enough to predict a band gap of 3.23 eV (see Fig. 1) for the 4 H-SiC, which is in agreement with the experimental value of 3.26 eV at 300 K [52]. The 4 H-SiC has a hexagonal cubic structure with the space group P_6_3mc for its unit cell. The optimized lattice constants and band gap for the 4 H-SiC unit cell were obtained using a Monkhorst-Pack [53] grid of 8 × 8 × 8. A kinetic energy cutoff of 400 eV was used for the expansion of one-electron Kohn-Sham wave functions on the plane-wave basis. Furthermore, the cell was relaxed until the minimum total energy difference was less than 10^{-5} eV. Equilibrium configurations of all the atomic geometries were allowed to relax freely until the Hellmann-Feynman forces acting on each atom was less than 0.01 eV/Å. The calculated lattice parameters a = 3.07 Å, c = 10.05 Åand c/a = 3.27, are in good agreement with experimental values of 3.07 Å, 10.05 Åand 3.27 [52,54], respectively. Defect calculations are suitably performed using periodic supercell with boundary conditions. For the defect calculation, a 2 × 2 × 2 supercell of 96 atoms containing 48 each of Si and C atom was created from the repeated optimized unit cell. The supercell atomic positions were relaxed using the same convergence criteria as of the unit cell but with a reduced 2 × 2 × 2 Monkhorst-Pack k-point grid. More information about the convergence criteria of the supercell can be found in our previous report [26]. Inside the supercell, a P atom was substituted at either C or S atomic site and a C or Si vacancy was created to form a P related vacancy-complex. This same procedure was repeated for the Al related vacancy-complexes. This is followed by atomic relaxation with the same conditions as the pristine 96 atoms supercell of the 4 H-SiC. Spin polarization was included in all calculations involving $\mathrm{V_{Si}}$, this is to account for the spin dependency of $\mathrm{V_{Si}}$ [55–57]. A vacancy-complex formation energy $E^F(vacancy-complex, q)$ as a function of electron Fermi energy (ε_F) is given as [58,59]

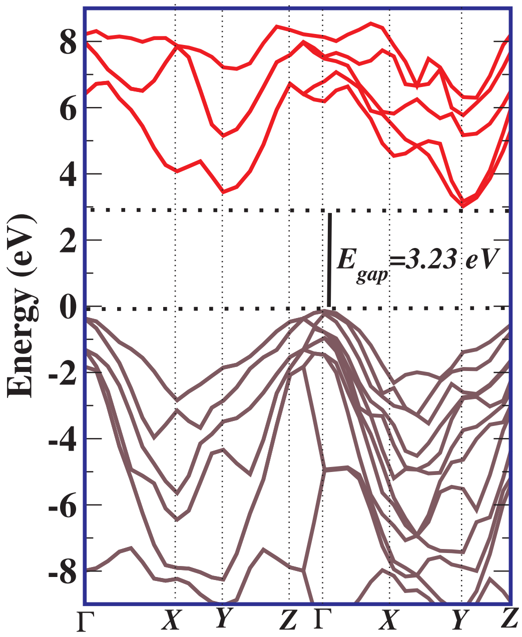

Fig. 1. Band structure of 4 H-SiC using the HSE06 hybrid functional. The band gap E_{gap} is 3.23 eV.