Studies of Molecular Dynamics and Electronic Structure in Cubic-SiC by Using Density Functional Tight Binding Approach

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ARTICLE INFO	ABSTRACT
	The radiation damage in Silicon-Carbide and its result are presented in this research. The Density Functional Tight Binding (DFTB) approach is used to perform molecular dynamics simulations to implement the DFTB+ code (Elstner et al., 1998). This methodology shows the making and breaking of chemical bonding as well as describes the realistic total energy for the larger systems. Repulsive potentials have been developed to prevent the atoms to stay close to each other during the model of high energy collisions also correctly describe the configurations during the atomic separation within the typical range. The extent and nature of damages are characterized within the collision event up to 10KeV. The band structure of SiC has been studied using minimal basis (sp) as applied in DFTB+. The value of band gap shows that cubic SiC is a large band gap semiconductor material. This value is comparable with the given in literature. Density of states is also calculated by using the tight binding approach. The peaks of spectrum have been compared with the experimental values found in literature.

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1. Introduction

Silicon Carbide is a well-known material in semiconductor technology. It is used as a nuclear fuel for fusion reactors. The aim of current research is to study the radiation damage and electronic structure in SiC by using the density functional tight binding approach. The density functional tight binding scheme is more accurate than empirical tight binding methods. The basic structural unit in SiC consists of four Si (or C) atoms are connected by the covalent bond with a C (or Si) atom at the centre. SiC is mostly used in electronic devices due to its strong chemical bonding, physical stability, and other attractive electrical, optical, and thermal properties. Detailed knowledge of electronic structure is essential to explain the applications of this material (Käckell, Wenzien, & Bechstedt, 1994). Tight Binding models are very successful to the study both semiconductor and metallic systems especially in systems which are too large to study via ab initio techniques. Despite the successes of TB models, TB approach has some limitations one of these is the treatment of compound or multi-elemental systems (Mercer, 1996). Gao et al investigated the long-range migration of points defects in cubic SiC by using atomic-scale simulations for molecular dynamics. They calculated the activation energy of migration barrier for C and Si interstitials and this energy was compared with the experimental results. They also compared the energy barrier for C interstitial and vacancy diffusion with ab intio data (Gao, Weber, Posselt, & Belko, 2004). Rauls et al has used the self-consistent-charge density functional-based tight binding theory to investigate the migration of vacancies at high temperatures along with the entropy contribution to Gibbs free energy. They found the energy barrier for sub lattice migration of V_{Si} is lower than that for V_C whereas V_{Si} should anneal out at low temperature, which was consistent with experimental results for as grown SiC (Rauls, Frauenheim, Gali, & Deák, 2003). Bernstein et

al used Naval Research Laboratory nonorthogonal tight binding method to present the electronic structure and total energy calculations for SiC. They compared the energies of different structures of silicon carbide. They described the elastic constant and vacancy formation energies for the cubic structure by using sp tight binding model and showed the good agreement of theoretical and experimental results (Bernstein, Gotsis, Papaconstantopoulos, & Mehl, 2005).

Mahmood et al used the density functional and total energy pseudopotential technique under the generalized gradient approximation to study the electronic structure in zinc-blende SiC. They compared their results about energy gap theoretically and experimentally. They also calculated the density of state, charge density and bulk modulus of cubic silicon carbide (Mahmood & Sansoresa, 2002). Demkov et al used an ab initio method to determine the microscopic atomic structure of Si-C alloys. They determined the effect of ordering using the plane wave calculation on the ordered structures. They found two different types of Si-C bonds. The first type of bond was the Si-C bond of the length near 1.86 Å as in bulk and the second type of bond was about 1.65 Å for a carbon atom in a near-planar sp^2 configuration with its Si neighbours (Demkov & Sankey, 1993). Salvador et al showed that tight binding approach is a quite effective description of inter-atomic bonding especially dealing with covalent bond of materials.They described the physics of point defects on the basis of making and breaking of bond and discussed the defects energetics in β-SiC by using tight binding model (Salvador, Perlado, Mattoni, Bernardini, & Colombo, 2004).

2.   Density Functional Tight Binding Theory

The modern tight binding approach has an origin in the Slater and Koster's important paper (Slater & Koster, 1954). The concept of Linear Combination of Atomic Orbitals (LCAO) has been used to develop the rapid, robust, generally transferable and accurate methods for the calculation of atomic and electronic structure, energies and forces of large and complex systems.

In order to use the DFT practically, the Kohn-Sham orbitals $\Psi_i(r)$ are required to expand some way. Majority of basis set expansion of the Kohn-Sham orbital Ψ_i can be expanded in term of suitable basis functions $\chi_\mu(r)$

$$\Psi_i(r) = \sum_{\mu=i} C_{\mu i} \chi_\mu(r) \tag{1}$$

The Eigen states of a system were expended using standard Tight Binding methods to represent the exact many-body Hamiltonian operator in terms of an orthogonalized basis of the atomic like orbitals. LCAO ansatz leads to secular equation in the form:

$$\sum_v^M c_{\mu v} \left(H_{\mu v}^0 - \epsilon_i S_{\mu v} \right) = 0, \forall \mu, i, \tag{2}$$

Total energy expression of the system can be written as the sum of band structure energies and repulsive energies (Frauenheim et al., 2000).

$$E = E_{bs} + E_{rep} \tag{3}$$

The DFT total energy is transformed into TB form including the charges fluctuation (Porezag, Frauenheim, Köhler, Seifert, & Kaschner, 1995)

$$E_2^{TB} = \sum_i^{occ} \left\langle \Psi_i \middle| \hat{H}_O \middle| \Psi_i \right\rangle + \frac{1}{2} \sum_{\alpha,\beta}^N \gamma_{\alpha\beta} \Delta q_\alpha \Delta q_\beta + E_{rep} \tag{4}$$

By applying the variational principle to energy functional eq.4,Kohn-Sham equation transformed in to set a algebraic equations and modified Hamiltonian matrix elements can be written as (Porezag et al., 1995):

$$H_{\mu v} = \left\langle \phi_\mu \middle| \hat{H}_O \middle| \phi_v \right\rangle + \frac{1}{2} S_{\mu v} \sum_\xi^N (\gamma_{\alpha\xi} + \gamma_{\beta\xi}) \Delta q_\xi = H_{\mu v}^o + H_{\mu v}^1 \; ; \forall \; \mu \in \alpha, v \in \beta \tag{5}$$

An analytic expression for the inter atomic forces for the use in molecular dynamics simulations can be derived by taking the derivative of the expression of eq.4 with respect to nuclear coordinates.

$$F_\alpha = -\sum_i^{occ} n_i \sum_{\mu\nu} c_{\mu i} c_{\nu i} \left(\frac{\partial H_{\mu\nu}^0}{\partial R_\alpha} - \left(\epsilon_i - \frac{H_{\mu\nu}^1}{S_{\mu\nu}} \right) \frac{\partial S_{\mu\nu}}{\partial R_\alpha} \right) - \Delta q_\alpha \sum_\xi^N \frac{\partial \gamma_{\alpha\xi}}{\partial R_\alpha} \Delta q_\xi - \frac{\partial E_{rep}}{\partial R_\alpha} \qquad (6)$$

3. Results and Discussion

Neighbours in 64 atoms supercell got too close to each other on bombarding the high radiation up to 10KeV as shown in figure 1. Repulsive potentials was developed to avoid atoms un-physically get too closed by using self consistent density functional-based tight binding (SCC-DFTB) approach as shown in figure 2. Exponential part of repulsive potentials were smoothly joined with spline part of repulsive at the inter atomic distance R=1.0 a.u. (atomic unit). The parameterization set pbc-0-3 was used to develop the repulsive (Köhler & Frauenheim, 2006; Köhler, Hajnal, Deák, Frauenheim, & Suhai, 2001; Rauls, Elsner, Gutierrez, & Frauenheim, 1999).

Figure 1: Neighbouring Si and C atoms are getting too close (0.2Å) in 64 atoms of SiC Supercell
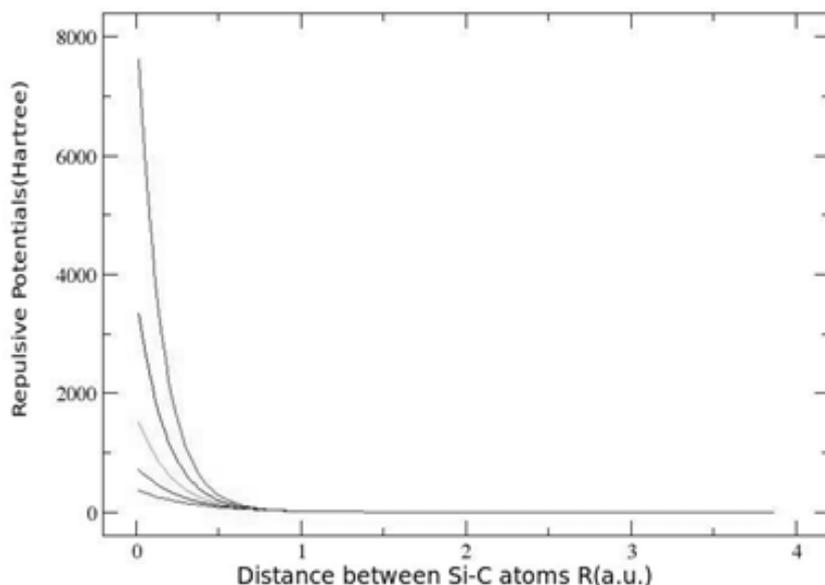

Figure 2: repulsive vs. Inter atomic distance by using the parameterization set pbc-0-3

Angle between C-Si-C atoms found from 109.5⁰ to 130⁰ during stretching. Bond length of Si-C of the value 2.32 Å was found before breaking as shown in figure 3. Jmol software was used to visualize the dynamics of atoms. Carbon atoms were shown by black small balls and silicon atoms are indicated by light gray balls. Figure 4 describes the correct description of DFTB modelling for making and breaking of bond in large super cell of silicon carbide. Time step of the value 0.01 fs was choosen corresponding to energy of radiation 2KeV. Initial value of high energy was dispersed with the change in crystalline to amorphous phase as shown in figure 5.
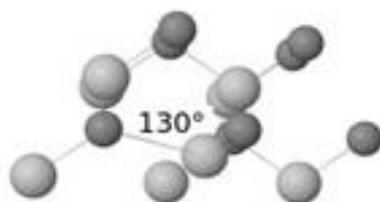
Figure 3: The bond angle between C-Si-C at the maximum streching of Si-C bonds
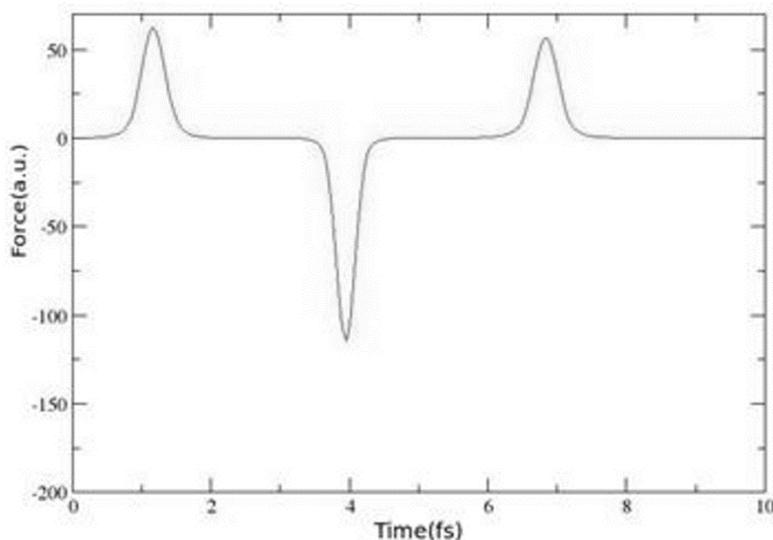

Figure 4: Variation of force with time using SCC-DFTB

During cascaded process, energy was shifted between first neighbours due to stretching and compressing the bond. Oscillatory behavior in distance between neighbours indicates the compressing and stretching of bond. As the intial value of bombarding energy was greater than Si-C bond energy caused the neighbouts reached too close near the boundary of cell.The nearest calculated distance between Si-C atoms was found at value of 0.2 Å. At this point, Hamiltonian matrix was failed to diagonalized at this postion.This point is marked by gray arrows in figure 6.

Table 1
Values of physical quantities calculated by SCC-DFTB for cubic SiC

a(Å)	V(a.u.)^3	E_{TOTAL}(H)	P(a.u.)
5.0334	861	-11.7241	-0.0013
4.7937	743	-11.8613	-0.0010
4.5654	642	-11.9400	-0.0005
4.3480	555	-11.9471	0.0007
4.1306	476	-11.7953	0.0031
3.9240	408	-11.4765	0.0066
3.7278	350	-10.9640	0.0115
3.5414	300	-10.2169	0.0192
3.3643	257	-09.1592	0.0315

Figure 5: The dispersing of initial 2KeV in 64 atoms supercell of SiC after 1000 steps at time step 0.1fs
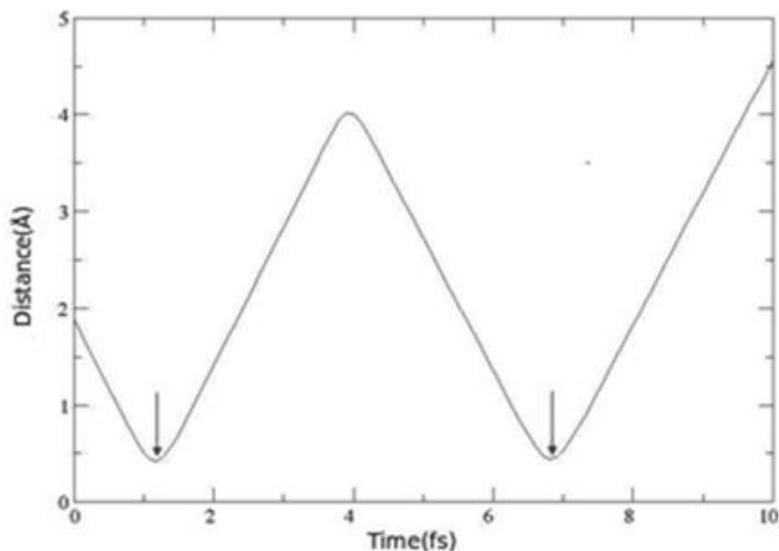
Figure 6: The change in distance between the nearest neighbour Si-C atom

Total Energy E_{TOTAL} in the units of Hartree (H) reaches the minimum value at the stable lattice constant a = 4.3480 Å as given in table 1 and experimental value of lattice constant is found a =4.343 Å (Rauls et al., 2003). Calculated values of pressure P increase with decrease in volume V of the system below the stable lattice constant a and become negative on increasing the volume V of the system.
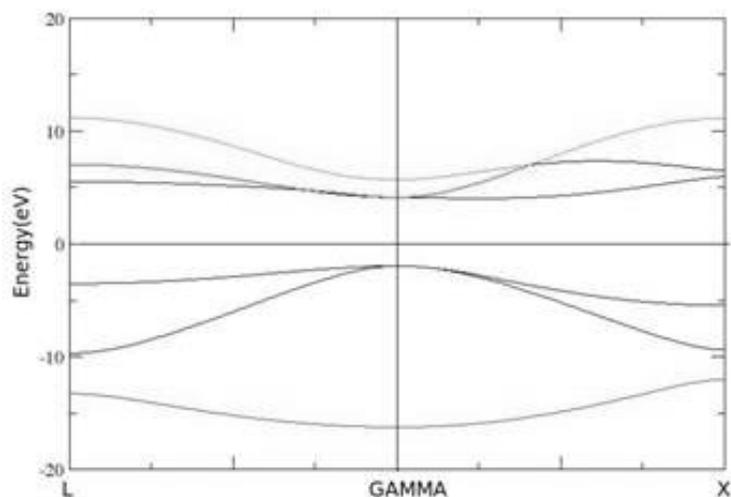

Figure 7: Band Structure of SiC Calculated by DFTB+ along L- Gamma-X line using the parameterization set pbc-0-3

Band Structure of SiC has calculated along the high symmetry L- Gamma-X directions in face centred cubic Brillouin Zone (BZ). In SCC-DFTB approach, the minimal basis (sp) leads to value of direct band gap 4.81eV at center of BZ as shown in figure 7. The calculated value of band gap is high as compared with experimental value 2.39eV (Park, Cheong, Lee, & Chang, 1994; Rauls et al., 2003). This shows that cubic SiC is a large band gap material. First two bands in conduction band degenerates and splits as move toward the L-point and X-points. Density of states in arbitrary units are also calculated by using SCC-DFTB method. Peaks in valence band found at the values of energy-4.94eV,-6.23eV,-8.04eV,-12.01eV,-14.96eV,-16.25eV as shown in figure 8.These values of peaks are comparable with experimental values of peaks at -3.0eV,-5.0eV,-8.5eVand -12.8eV in a valence band respectively as mentioned by Karch et al (Karch, Pavone, Windl, Strauch, & Bechstedt, 1995). Conduction band has also three prominent peaks at the values of 1.60eV,2.73eV, 4.33eV respectively. The largest peak of density of states lies at 1.60eV in conduction band as shown in figure 8.
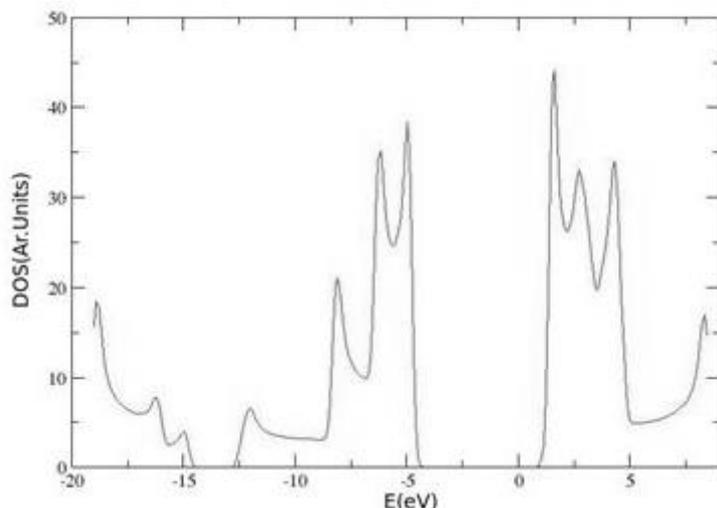
Figure 8: Density of states for SiC calculated by DFTB+ using the parameterization set pbc-0-3

4.   Conclusion

DFTB approach is useful to study molecular dynamics of the radiation damage up to 10KeV collision energy for large cubic SiC systems. At the minimum value of distance between nearest neighbours, molecular dynamics kinetic energy of the system is greater than pair potential energy. This is main reason of atoms getting too close. This problem was corrected by developing new repulsive potentials between nearest neighbours (Si-C atoms). DFTB approach also overestimates the value of band gap in cubic SiC system.

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