

Ability of a hydrogen atom to be adsorbed on the 2D silicon carbide

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Abstract. *Hydrogen bonding on two-dimensional silicon carbide (2D SiC) was studied using molecular dynamics and ab initio calculations. By investigating a converged density functional theory (DFT) calculation, the stable bonding sites of a hydrogen atom on the 2D SiC were found at the top sites (T_{Si} and T_C , of which T_{Si} is a more stable adsorption site). The adsorption investigation of the H/SiC system showed the local change in the SiC lattice. The calculated band gap is about 2.2 eV, which was compared with previous studies.*

Keywords: density functional theory calculation; two-dimensional; silicon carbide; hydrogen adsorption.

Classification numbers: 71.15.Mb; 88.85.mh; 77.84.Bw.

1. Introduction

After the success of creating graphene in 2004, two dimensional materials have attracted the attention of many research groups worldwide [1–5]. Many elements can form thin films, such as C, Ge, Si... It has been shown that the mixture of silicon (silicene) on a silver base has been synthesized in 2010 and 2012 [6,7]. Besides, by experimental methods such as the thermochemical reaction of Si powder at high temperatures, SiC cotton is almost 2D [8]. In theoretical studies, 2D SiC materials have been shown to have bond lengths from 1.77 Å to 1.89 Å with a large bandgap of about 2.5 eV [3, 9, 10]. Because of a large bandgap, the 2D SiC is expected to be of great significance in the application of nano-devices for use under both high conditions of temperature and frequency.

By using different simulation methods in theoretical studies, like molecular dynamics (MD) and density functional theory (DFT) methods, it has been shown that different bond length values lead to a change in the properties of 2D silicon carbide models [11–13]. However, many properties of 2D SiC, such as hydrogen adsorption capacity, 2D SiC surface deformation, etc., have not been

studied yet. Therefore, in this study, by combining the two methods of MD and DFT studies, the 2D SiC model is revisited. Using the MD simulation, the pristine 2D SiC model is studied. Then, by using the DFT calculation with the convergence controlled, the H – SiC interaction of the 2D H/SiC is investigated. The structural deformations of SiC when interacting with hydrogen are also investigated and studied in this paper.

2. Methodology

The 2D SiC model of 6000 atoms is constructed by using the MD simulation via the LAMMPS package (Large-scale Atomic/Molecular Massively Parallel Simulator). The LAMMPS simulation software is a MD program that focuses on materials modeling [14]. We use the conditions of periodic boundary and Vashishta potential [15]. To investigate whether when crystallizing from this interaction potential, the obtained model has better hydrogen adsorption than the theoretical models generated directly from the DFT of other studies, the DFT calculation is conducted.

To obtain the optimized structures and the ground-state energies of all MD-obtained simulation models, the DFT method is used via the SIESTA software [16]. The GGA, PBE functional, the 200 Ry energy cutoff, the periodic boundary condition, and the basis sets of DZP are used for all simulation models. The periodic distance in the z-axis is 40 Å, which is used for the purpose of ignoring most periodic side-layer interactions. When the maximum stress component is small enough (usually it is accepted to be less than $0.02 \text{ eV}\cdot\text{Å}^{-1}$), the geometry optimization loop is stopped. To decide to choose the above parameters, several previous studies have verified the reasonableness and accuracy of the obtained results [17, 18]. From the obtained MD simulated structure, a SiC supercell of 98 atoms is cut out. Then, a hydrogen atom is put on the 2D non-fixed SiC surface to determine the stable site of the H/SiC adsorption system. To check the k-point convergence, the k-point grid from 0 to $(13\times 13\times 1)$ MP scheme is taken into account.

3. Results and discussion

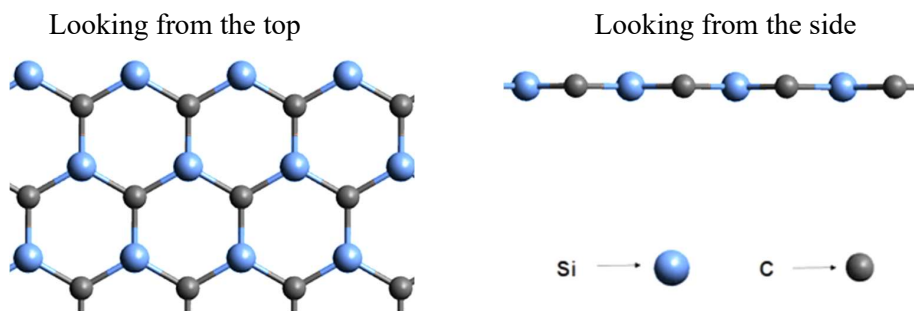


Fig. 1. The obtained 2D silicon carbide model.

The MD results show that the relaxed bond length between silicon and carbon atoms of the optimized solid silicon carbide model at 300K is 1.85 Å. This bond length is close to 1.89 Å found in the study of [19]. No buckling is found in the SiC model (see Fig. 1), as expected from the previous research [20].

From the obtained structure of 6000 atoms, a smaller model of 49 silicon and 49 carbon atoms is analyzed. The DOS of this system is shown in Fig. 2. This DOS result shows that the SiC model has semiconductor properties, similar to the results of some previous studies [9, 10].

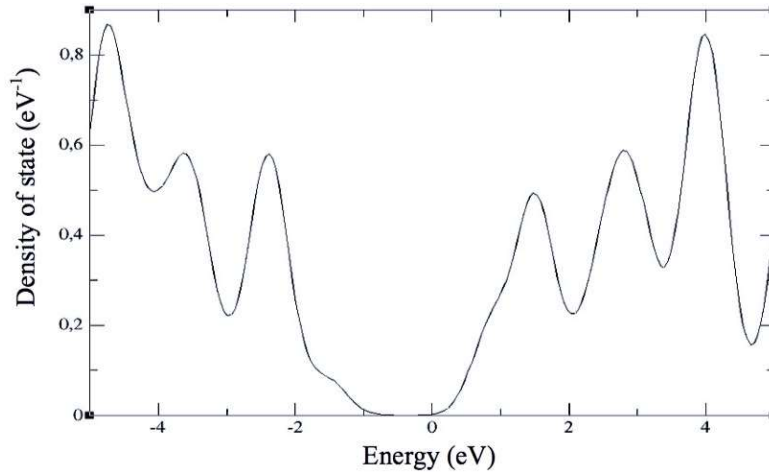


Fig. 2. The density of state of the 2D silicon carbide model.

To further verify the electrical properties of this model system, the bandgap has been calculated through Fig. 3. The obtained bandgap of ~ 2.2 eV is smaller than the previous studies' result (2.5 eV) [3, 9, 10]. This can be explained by the difference in bond lengths between the Si and C atoms. The bond length obtained from the MD calculation for more than 6000 SiC atoms is 1.85 Å, while the commonly seen bond length of the 2D SiC is 1.79 Å [3, 10]. In addition, the bandgap energy of the 2D SiC model is smaller than that by other calculations which may be due to the fact that the PBE pseudopotential often calculates a smaller band gap energy than it is in experiment [21].

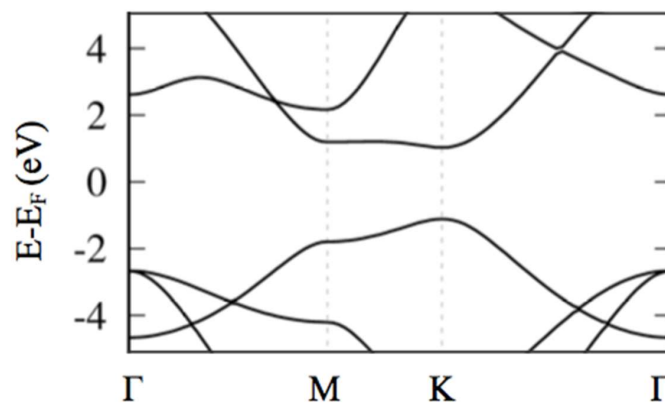


Fig. 3. The band structure of the 2D silicon carbide model.

Then, the H atom is randomly dropped on different positions on the silicon carbide surface: 02 top, 01 bridge, and 01 center sites. After optimizing the system, only the top sites (T_C , T_{Si}) exists (see Fig. 4). Ivanovskaya *et al.* also show similar results in the graphene model [22]. To check the convergence of the k-point value, the energies of adsorption T_C and T_{Si} systems are found when the k-point value changes (see Table 1 and Fig. 5). It shows that from the k-point value of the $(3 \times 3 \times 1)$, the magnitude of the changes in the adsorption energy is less than 0.005. This means that the convergence is obtained for the k-point. Therefore, to study the H/SiC system, the k-point of $(3 \times 3 \times 1)$ is chosen.

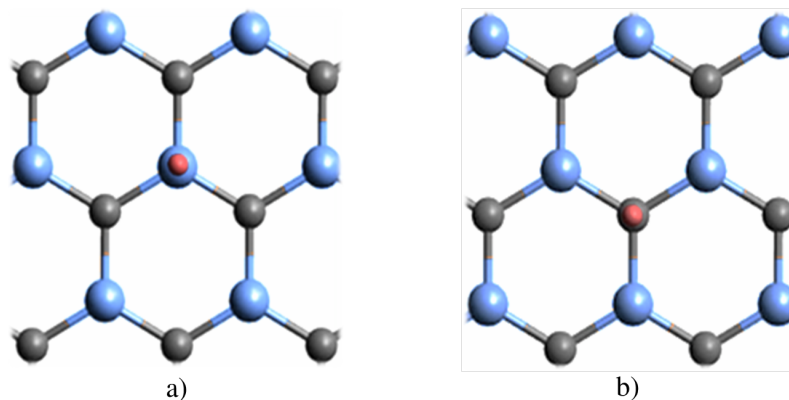


Fig. 4. The red hydrogen atoms are on a) the top T_{Si} and b) the top T_C positions.

The formula used to calculate the adsorption energy E_{ads} is:

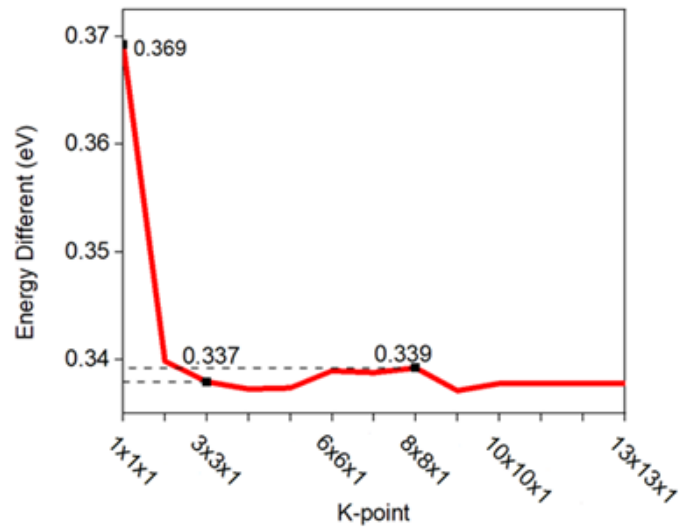
$$E_{ads} = E(H/SiC) - E(SiC) - \frac{1}{2}E_{H_2},$$

where E_{ads} is the hydrogen adsorption energy on 2D SiC, $E(H/SiC)$ is the energy of the model of one H on the 2D SiC, $E(SiC)$ is the SiC energy, and E_{H_2} is the hydrogen molecule's energy. It is found that $E_{ads(T_{Si})} = -0.71$ (eV), and $E_{ads(T_C)} = -0.37$ (eV). This result indicates that the more stable adsorption site is the Si site.

Figure 6 displays the SiC lattice distortion around the hydrogen adsorption position. Because we cannot observe the distortion from the z-axis view, it proves that the displacements in the x- and y-axis are small. Table 2 shows the displacement of Si and C atoms when a hydrogen atom is adsorbed on the SiC surface. The numbering in Table 2 is corresponding to Fig. 6. The results show that the hydrogen atom attracts the carbon atom higher than the Si atom along the z-axis does at the absorption point ($z_C=0.460$ Å, $z_{Si}=0.369$ Å). In addition, the hydrogen atom also attracts the first neighboring silicon atoms upwards, causing the 2D SiC film to form local deformation at the adsorption site on the C atom (Table 2). Previous theoretical work on graphene also noted this property [22]. In contrast to the obvious observation of local deformation at the adsorbent C atom, the adsorbent silicon local deformation is almost not found (Table 2). This once again confirms that the silicon atoms bonded to the SiC lattice are more stable. And the results in Table 1 are also consistent with this conclusion.

Table 1. The E_{ads} (eV) of the H/SiC monolayer model on the different T_{C} , and T_{Si} sites.

k-point	top C	top Si
$(1 \times 1 \times 1)$ MP	-0.34643	-0.71564
$(2 \times 2 \times 1)$ MP	-0.37178	-0.71165
$(3 \times 3 \times 1)$ MP	-0.37375	-0.71170
$(4 \times 4 \times 1)$ MP	-0.37410	-0.71138
$(5 \times 5 \times 1)$ MP	-0.37373	-0.71111
$(6 \times 6 \times 1)$ MP	-0.37302	-0.71199
$(7 \times 7 \times 1)$ MP	-0.37272	-0.71151
$(8 \times 8 \times 1)$ MP	-0.37274	-0.71197
$(9 \times 9 \times 1)$ MP	-0.37391	-0.71103
$(10 \times 10 \times 1)$ MP	-0.37377	-0.71156
$(11 \times 11 \times 1)$ MP	-0.37377	-0.71156
$(12 \times 12 \times 1)$ MP	-0.37377	-0.71156
$(13 \times 13 \times 1)$ MP	-0.37407	-0.71187

**Fig. 5.** The convergence of the k-point (the energy difference is $E_{\text{ads}}(T_{\text{C}}) - E_{\text{ads}}(T_{\text{Si}})$).

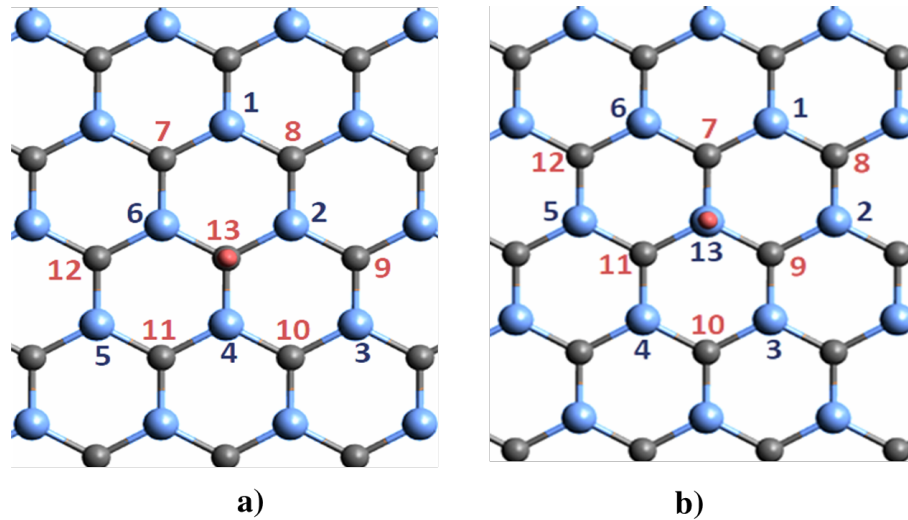


Fig. 6. There are no distortions observable in the 2D SiC supercell when viewing from the top. The H atom was marked with red color in both adsorption configurations T_C (a) and T_{Si} (b). The neighborhoods of the adsorbent atom are numbered to correspond with Table 2.

Table 2. The displacement of non-fixed 2D SiC atoms with a hydrogen atom adsorbed on the top sites compared with the optimized model (Å). First-order neighborhoods of the adsorbent atom have been in boldface.

		T_C			T_{Si}				
	Atom	x	y	z	Atom	x	y	z	
1	Si	0.016	0.017	0.011	Si	0.014	0.011	0.014	
2	Si	0.087	0.021	0.066	Si	0.006	0.018	0.014	
3	Si	0.025	0.014	0.013	Si	0.011	0.001	0.015	
4	Si	0.004	0.072	0.058	Si	0.017	0.006	0.014	
5	Si	0.001	0.008	0.014	Si	0.013	0.016	0.014	
6	Si	0.037	0.050	0.061	Si	0.006	0.004	0.014	
7	C	0.012	0.014	0.003	C	0.002	0.029	0.004	
8	C	0.020	0.012	0.006	C	0.008	0.003	0.011	
9	C	0.027	0.005	0.010	C	0.017	0.020	0.006	
10	C	0.020	0.014	0.004	C	0.003	0.002	0.011	
11	C	0.008	0.009	0.007	C	0.034	0.009	0.005	
12	C	0.004	0.001	0.009	C	0.004	0.004	0.011	
13	C	0.017	0.000	0.460	Si	0.005	0.001	0.369	

4. Conclusions

The possibility of hydrogen bonding with 2D silicon carbide films has been investigated through the theoretical simulation method. The results show that there exist the bonding sites of hydrogen atoms on 2D SiC which are the on-top sites T_{Si} and T_C , of which the more stable adsorption position is T_{Si} . The binding of a hydrogen atom to a 2D silicon carbide surface distorts the silicon carbide film structure. The C atom is pulled up along the z-axis at the hydrogen-carbon interaction site. This displacement of the C atom is larger than that of the Si atom, which indicates that the silicon atoms are more tightly bound to the 2D SiC lattice.

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