

# Systematic Theoretical Investigation for Adsorption Behavior of Several Small Molecular on SiC Surface

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**Abstract**—Based on the first-principles pseudopotentials and the plane wave energy band method, the adsorption behaviors of CO, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> molecules on  $\beta$ -SiC surfaces have been investigated in this paper separately. The results show that with ignoring the atomic relaxations and the temperature kept at 0K, when the molecule replaced the crystal lattice location connected with the unsaturated bond and except N<sub>2</sub> the molecules can be adsorbed on the Si atoms face of  $\beta$ -SiC crystal model, meanwhile all the bond distance of molecule changed because of the molecules' location difference and the max variation molecule belong to O<sub>2</sub>. Based on the energy of adsorption and rejection, the easiest adsorbed molecule is O<sub>2</sub> and then the H<sub>2</sub> and CO molecule, which supply somewhat effecting or influence on the conditions of preparation and storage of high quality SiC crystal. Meanwhile, The absorbing energy of CO, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> on SiC surface is 2.984eV, 2.415eV, 2.659eV, 8.7845eV, while the exclusion energy between CO, H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> reaches 2.965eV, 2.246eV, 2.872eV, 6.5635eV.

**Index Terms**—SiC surface, adsorption, density of State, small molecule

## I. INTRODUCTION

SiC (Silicon carbide) has outstanding device potential for high power, high voltage, high temperature and high frequency applications because it can be used as substrates for high-power, high-frequency devices based on SiC and GaN [1]. In addition, high-quality semi-insulating SiC crystals can also be applied in device isolation or junction termination, which is very important for improving the performances of devices. It is well known the State on surface of devices that effects the electrical characters and transport characters of carriers [2-6]. Among the defects, there are some differences in their energy level, thermal stability, concentration and so on. B. Wen et al [7] studied the lattice parameters, energy band structure and stability characters among different SiC crystals by first-principal. J. J. Wang et al [8] researched the First-principles investigation on initial stage of 2H-SiC surface oxidation, and so on.

Due to the high cost of SiC crystals at present, and the verifiable results of theoretical calculation, the prediction of SiC crystal defects is progressing more rapidly. As early as 1994 L. W. Chang et al [6] nitrogen were analyzed on SiC surface adsorption properties N main and Si surface,

not easy adsorption of C, Si, N can be chemically stable insulation used in electronic devices. Xu Peng shou, Liu Fu [9,10] are calculated SiC (2 $\times$ 1) think the table surface structure properties like cash. Y.M.Zhu et al simulated the physical and chemical characteristics of the surface of silicon carbide quantum dots and believed that -COOH and -OH functional groups formed stable chemical bonds on the surface. Wang fang fang et al [11] analyzed the interfacial state mechanism of silicon carbide on the basis of previous studies, and verified that the intrinsic defect in SiC MOS structure was a major source of interfacial state during the period of causing impurities, which was unrelated to impurities. Secondly, it indicates that the surface suspended bond or unsaturated bond is not the main source of the interface state, and the C cluster or residual C atom class donor interface state on the surface will become the class acceptor interface state when the size of the cluster is large. When interfacial silicon atoms are enriched, such defects can be theoretically passivated by N and H.

CVD method is a kind of preparation methods of high quality SiC crystals, produces in the process of preparation or H<sub>2</sub>, N<sub>2</sub>, O<sub>2</sub> and CO will happen in the process of storage or transportation, the small molecule gas such as O<sub>2</sub>, N<sub>2</sub>, contact, in order to analysis the common gas molecules on the surface of the SiC, adsorption, and provide theory for SiC crystal surface atomic structure possible structure model, combining with the existing research results, on SiC Si surface adsorption of H<sub>2</sub>, CO, O<sub>2</sub>, N<sub>2</sub>, four kinds of small molecule theory analysis, designed to provide the basis for subsequent analysis of interface states.

## II. DETAIL OF CALCULATION AND MODEL

The quantum mechanical program CASTEP was employed to perform the geometry optimization calculation in this paper. The generalized gradient approximation (GGA) for the exchange correlation energy was chosen. The lattice parameters come from experiment and the total energy calculations are in the reciprocal space k. Valence electron configurations of Si and C were selected as 3s<sup>2</sup>3p<sup>2</sup> and 2s<sup>2</sup>2p<sup>2</sup>, respectively. In this calculation, the accuracy of convergences was 1 $\times$ 10<sup>-5</sup> eV/atom in the iterative program with cut-off energy (Ecut) of plane wave adopted 280 eV in the reciprocal space k, and Monkrs-Park method was used to selected k points during the integral calculation in the Brillouin zone. The

optimization convergence for maximum stress and maximum displacement was set at 0.1 GPa and 0.002 Å,

respectively. The optimization step stopped until all the convergence conditions were satisfied.

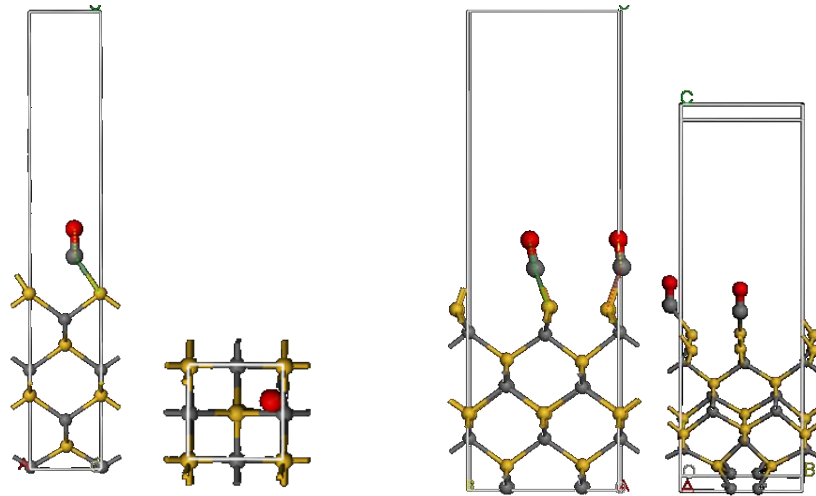


Figure 1. The structure of  $\beta$ -SiC and small molecular adsorption on its surface.

Figure 1 shows the diagram of adsorption position of single or two small molecular on SiC surface one and two. In Figure 1 the schematic diagram of four different small molecules adsorbed on the surface of SiC, with the vacuum layer value of 10 nm. The adsorption position of atoms is based on ensuring the integrity and regularity of crystal structure, and includes both boundary position and internal position. It can be seen from Figure 1 that, for the atomic surface of  $1 \times 1$ , the adsorption position of the single atom is taken as the position where the atoms are connected in the body in order to reduce errors, while for the atomic surface of  $2 \times 1$  and the bimolecule adsorption, the molecules can be placed at the critical positions in the body and the boundary respectively to judge the molecular change characteristics.

### III. RESULTS AND DISCUSSION

#### A. Calculation of Adsorption Energy

Based on the first-principle, the CO molecule, SiC, ( $1 \times 1$ ) CO on SiC surface and ( $2 \times 1$ ) CO on SiC surface have been computed. The total energy of each structure shows in table 1.

As can be seen from table 1, after the optimization of CO, H<sub>2</sub>, O<sub>2</sub> and N<sub>2</sub>, the distance between the atoms of the four small molecules increases, and the distance between

the N atoms has the largest error with the experimental data, but the error is within the error range allowed by CASTEP simulation software. When a small molecule is adsorbed on the crystal surface of beta-SiC, a single molecule is adsorbed on the suspended bond at the center of the crystal surface, and the intermolecular bond length increases, among which the h-h bond increases the least and the o-o bond length increases the most. This is mainly due to the degree of affinity between Si and C atomic bases to different atoms, except for errors caused by the optimization process. When bimolecules are adsorbed on the crystal surface of beta-SiC, from the perspective of the bond length between the adsorbed molecules, compared with the optimized bond length, the bond length of molecules adsorbed on the boundary, except that the bond length of H-H and C-O bonds remains basically unchanged, O-O and N-N bonds, especially the increasing trend of O-O bond length; The molecules adsorbed into the body are C-O bond and N-N bond bond length slightly increased, O-O bond and H-H bond length remained basically the same trend. The possible reason for this phenomenon is that there are more unsaturated bonds at the center of the molecule, and the force between atoms is larger, resulting in shorter central molecular bonds.

Table 1. The bond length results of different absorptive molecule.

Small molecular name	CO	N <sub>2</sub>	O <sub>2</sub>	H <sub>2</sub>	
The bond of model (Å)	1.128	1.095	1.208	0.741	
After calculation (Å)	1.155	1.160	1.242	0.753	
Absorption with single molecule (Å)	1.176	1.177	1.343	0.754	
Double molecule (Å)	boundary	1.159	1.203	3.121	0.754
	inner	1.185	1.189	1.240	0.753
The error between optimization (%)	2.4	5.9	2.8	1.6	

The SiC surface was optimized using fixed the bottom atoms, and the top atom is free. The CO and others adsorption position comes from the crystal structure of the C atom location, the C atoms on the basis of O atoms

$$\Delta E_{\text{chem}} = 0.5 \times E_{(2 \times 1)\text{CO on SiC}(001)} - E_{\text{SiC}(001)} - E_{\text{CO molecule}}$$

vertical surface. The bond length of CO is determined by the optimized CO molecular.

Then the adsorption energy of CO and others on SiC can be deduced by Equations (1) and (2).

$$(1)$$

$$\Delta E_{rep} = 0.5 \times E_{(2 \times 1)COonSiC(001)} - E_{(1 \times 1)COonSiC(001)} \quad (2)$$

There  $\Delta E_{chem}$  is the adsorption energy of CO and other molecule on SiC (001) surface, the exclusion energy between CO and others molecule express by  $\Delta E_{rep}$ .

Table 2. The results of absorptive energy among different molecule.

molecule	CO	H <sub>2</sub>	O <sub>2</sub>	N <sub>2</sub>
System Energy (eV)	-589.907	-31.671	-866.623	-541.273
Single Molecule	-1635.152	-1077.066	-1914.070	-1586.331
Double Molecule	-3276.234	-2158.624	-3841.267	-3178.316
Absorptive energy (eV)	-2.984	-2.415	-8.7845	-2.659
Rejection Energy (eV)	-2.965	-2.246	-6.5635	-2.827

When CO molecule is adsorbed on SiC surface, its adsorption energy is -2.984 eV, and its rejection energy is -2.965 eV, that is, the adsorption energy value is greater than the rejection energy value, but the difference is not large, the results show that CO molecule can be adsorbed on SiC surface. When O<sub>2</sub> molecules are adsorbed on SiC surface, the repulsion energy value is less than the adsorption energy value, and the difference between the repulsion energy and the adsorption energy is 2.221 eV, indicating that O<sub>2</sub> molecules can be adsorbed on SiC surface. When H<sub>2</sub> molecules are adsorbed on SiC surface, the adsorption energy value is higher than the repulsive energy value, and the energy difference is 0.169 eV, indicating that H<sub>2</sub> molecules can be adsorbed on SiC surface. When N<sub>2</sub> molecule is adsorbed on SiC surface, its adsorption energy is -2.659 eV and its rejection energy is -2.827 eV. The rejection can is greater than the adsorption to numerical value, the difference between the energy of 0.372 eV, the results indicate that N<sub>2</sub> molecules cannot adsorption on the surface of SiC, result and LuWenChang et al. [6] the research results of large difference, known as N in SiC materials is a very important and common N type doping, the calculation first N atoms or molecules in beta-SiC surface does not exist in the form of adsorption, the results are consistent with the results of surface states. Secondly, the existence of N atoms or molecules in SiC crystals is more likely to be solid solution interstitial atoms than substituent atoms, and the concentration gradient will change with the increase of axial distance. In addition, when N exists as a molecule in SiC crystal and in the form of valence electron saturation, it affects the interaction force and mode of action between atoms, resulting in the phenomenon that it cannot be adsorbed on the suspended bond. From the perspective of adsorption energy, O<sub>2</sub> has the strongest adsorption capacity on the surface of beta-SiC, followed by H<sub>2</sub>, and finally CO, while N<sub>2</sub> as a substituent does not adsorb on the surface of beta-SiC.

It can be seen that H<sub>2</sub> molecule located on SiC surface needs higher energy meanwhile the distance should keep away from the adsorption and exclusion energy.

### B. Density of State

In this section the adsorptions of H<sub>2</sub> molecule on the SiC surface are investigated. Four adsorption sites are considered in present work. Figure 2 shows the density of state of H<sub>2</sub> molecule. Figure 3 is the density of state of

(2×1) H<sub>2</sub> molecule on SiC surface. Figure 4 expresses the part density of state of one H<sub>2</sub> molecule on SiC surface.

In the Figures 2-4, the blue curve is the total density of state, the red curve expresses the ratio of P layer electrons and black curve shows the ratio of S layer electrons.

From the Figure 2 we can see that the electronic states of isolation H<sub>2</sub> molecular is concentrated in the -20, -5, 0, 11eV, in which the P layer electrons is the mainly donors. In Figure 3, Electronic distribution mainly concentrates in the two regions, one is located at -23-25eV, the other is located in a broad region -17-6eV and the donors is the same than that of H<sub>2</sub> molecule. On the other hand Figure 3 shows the features of metal, so that the SiC surface adsorption H<sub>2</sub> molecules for semiconductor devices has a fatal injury. From Figure 4, the part density of state of one H<sub>2</sub> molecule on SiC surface, H<sub>2</sub> molecular electronic distribution changed significantly, and the electron distribution of H<sub>2</sub> molecule is the roughly same as that of adsorption system, which are mainly distributed in two regions, one of which is from -23 to -25eV, another is a wide area from -14 eV to 5eV. Contrast with Figure 2, the electronic distribution area of H<sub>2</sub> molecule mobiles from high energy to lower.

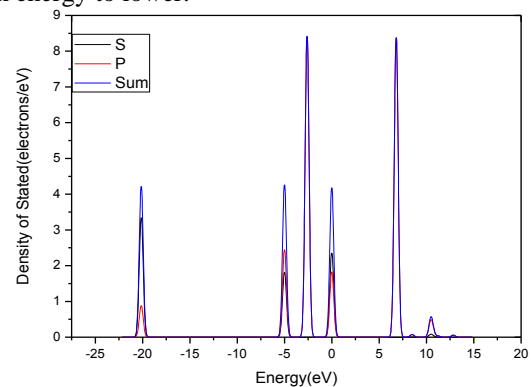


Figure 2. The density of state of H<sub>2</sub> molecule.

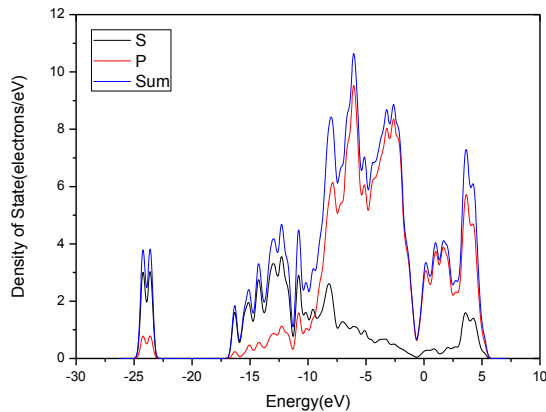


Figure 3. The density of state of  $(2 \times 1)$   $H_2$  molecule on SiC surface.

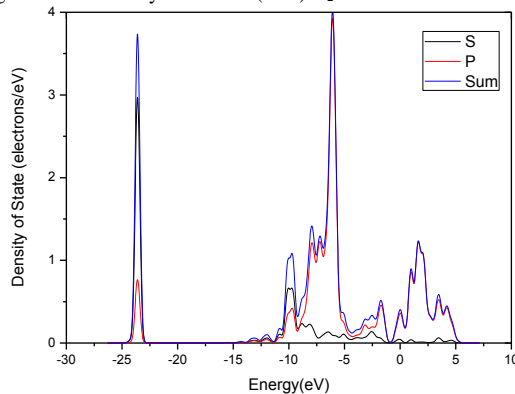


Figure 4. The part density of state of one  $H_2$  molecule on SiC surface.

As illustrated in Figures 2-4,  $H_2$  molecule adsorption on  $\beta$ -SiC surface make the semiconductor has metal characters. The  $H_2$  molecule adsorption on  $\beta$ -SiC surface has a significant effect.

In order to complete these results, the surface diffusion events of a CO adaptor are investigated by calculating the energy barriers to be overcome when jumping among different adsorption locations. By means of the NEB method, the minimum energy path (MEP) connecting the initial and final state of each diffusion process can be found. The initial and final states correspond to the optimized adsorption geometries obtained before.

#### IV. CONCLUSION

The adsorption behaviors of molecules on SiC surfaces have been researched employed the first-principles pseudopotentials and the plane wave energy band method in this paper. The calculations for stable adsorption site demonstrate that the molecule is adsorbed at the lattice site of SiC. The molecules adsorption on SiC surface make the semiconductor has metal characters. The molecules adsorption on SiC surface has a significant effect. On the premise of ensuring the crystal integrity, CASTEP simulation software based on plane wave expansion and the first principle pseudopotential method was used to calculate the Si surface crystals of SiC surface and the supercells of  $H_2$ ,  $N_2$ ,  $O_2$  and CO small molecules that may be adsorbed. After optimization, the bond length of the small molecule model tends to increase. Considering the error in the simulation process and the difference

between the test condition and the simulation condition, the influence of the error is ignored in the simulation process. When the simulation condition is 0K and atomic relaxation is ignored, the lattice position is occupied by substituent adsorption, and the small molecules show a vertical relationship. The results show that, except  $N_2$ , other small molecules can be adsorbed on the Si surface of SiC. The results theoretically analyze that there is no n-containing second phase structure or structure in the surface state of SiC material. As the adsorption position of the four types of small molecules changes, the bond length of the small molecules all changes, among which, the intermolecular bond length with the largest  $O_2$  deformation at the boundary increases and the molecular and plane are basically parallel. From the perspective of adsorption energy,  $O_2$  has the strongest adsorption capacity on the surface of SiC, followed by  $H_2$ , and then CO.

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