



Electronic Properties of Silicon Carbide Nanosheet Under Hydrogen Adsorption: A DFT study

Najme Delavari

Department of Physics, K. N. Toosi University of Technology, Tehran, Iran
Email: ndelavari@mail.kntu.ac.ir

Mahmoud Jafari

Department of Physics, K. N. Toosi University of Technology, Tehran, Iran
Email: jafari@kntu.ac.ir

Abstract

This paper investigates the electronic properties of hydrogenated silicon carbide nano sheet based on the Density Functional Theory (DFT). All calculations have been performed using a plane-wave based pseudopotential method. First of all, we've simulate our hexagonal nanosheet of SiC. Then, we've tried different positions for hydrogen adsorption. Four different positions of adsorptions are considered in this paper and it is shown that the most stable state happens when hydrogen atoms are adsorbed on silicon and carbon atoms at the two opposite sides of silicon carbide hexagonal nano sheet. This adsorption have made some changes in the atoms positions so that the nano sheet didn't remain flat any more. The results have shown that this structure was the most stable one among those four, with a total energy about -346.12 Ry. Silicon carbide is a semiconductor with a wide band gap about 2.5851 eV. After the hydrogen adsorption, the hydrogenated silicon carbide nano sheet have has a band gap about 3.9499 eV, which is much more than the band gap in the pure structure.

Keywords: Silicon Carbide, Hydrogen Adsorption, Nano Sheet, DFT



Introduction

Hydrogen has been identified as one of the future energy carrier due to several inherent advantages including high energy density, light weight, no CO₂ emission, and abundant nature (Alper, 2003), (Cortright et al, 2002), (Jain et al, 2010), (Jain, 2009), (Winter, 2009). For the last three decades the efforts has been taken to find out suitable hydrogen storage materials with high hydrogen storage capacity and good hydrogen adsorption behavior. Among the various solid state options available, carbon nanostructures have been studied extensively due to its light weight, diversity in structures, large surface area and interesting hydrogen adsorption properties. Apart from the carbon nanostructure, another very promising hydrogen storage alternative is Si/SiC nanostructure (Lithoxoos et al, 2008), (Lan et al, 2009), (Ishihara et al, 2006). Si being in the same group with the carbon it shows properties quite similar to that of C. Again, as the polarizability of Si is more than C, so it is expected that, due to stronger van der Waal's interaction, SiC/Si nanostructures can bind hydrogen more strongly compared to the pure carbon nanostructures. (Mpourmpakis et al, 2006) have proposed that pure SiC nanotube can improve the binding energy with hydrogen molecule by 20% compared to pure carbon nanotube.

Owing to its exceptional thermal and physical properties (Choyke et al, 2004), silicon carbide (SiC) is a material, which is convenient for high temperature and high power device applications. Because of its wide band gap, SiC bulk structure has been a subject of active study in optical and optoelectronic research. Unlike the polymorphs of carbon, SiC is a polar material. In spite of the fact that both constituents of SiC are Group IV elements, charge is transferred from Si to C due to higher electronegativity of C relative to Si atom. Silicon carbide is a binary compound of carbon and silicon as widely used in electronic devices because of its high thermal conductivity, low density, high hardness, high mechanical strength, low thermal expansion coefficient, corrosion resistance and large band gap (Harris, 1992), (Ivanov et al, 1992), (Narushima et al, 1997), (Wang et al, 1999), (watari et al 2001).

So far different shapes of the SiC nanostructures have been made. As instance Dai et al (Dai et al, 1995) reported the first SiC nanorod synthesis by the reaction of carbon nanotubes with either silicon monoxide or silicon and iodine vapor. Meng et al (Meng et al, 1998) also synthesized the β -SiC nanorods using sol-gel method. As a wide band gap semiconductor, SiC was hopeful to be applied to optics and electronics.

Results and Discussion

The density functional theory (DFT) calculations were carried out using the Quantum Espresso Package. The Perdew-Burke-Ernzerhof (PBE) formulation of the generalized gradient approximation (GGA) was employed to describe the exchange and correlation energies.

It is generally accepted that quantum mechanics methods are very accurate in the study of nanostructures. This is because the electronic structure of molecules is taken into account in these approaches. That's why we have done our research based on the Density functional Theory.

First of all, we optimized the cutoff energy and the k-points for the pure Silicon Carbide nano sheet in order to simplify and save time. This optimization was made for the unit cell of the SiC nano sheet (consists of two atoms; one Si and one C) which can be generalized to the main structure. We found the optimized values of e-cut and K-Point are 80 Ry and $7 \times 7 \times 1$ respectively.



In this study we've used $4 \times 4 \times 1$ supercell of SiC nano sheet, which consists of 32 atoms (16 Si atom and 16 C atom). In addition, a 15 Å vacuum which is enough to isolate the single SiC sheet was added to the super-cell. In Fig. 1 we have shown the optimized structure of the SiC nano sheet from top view.

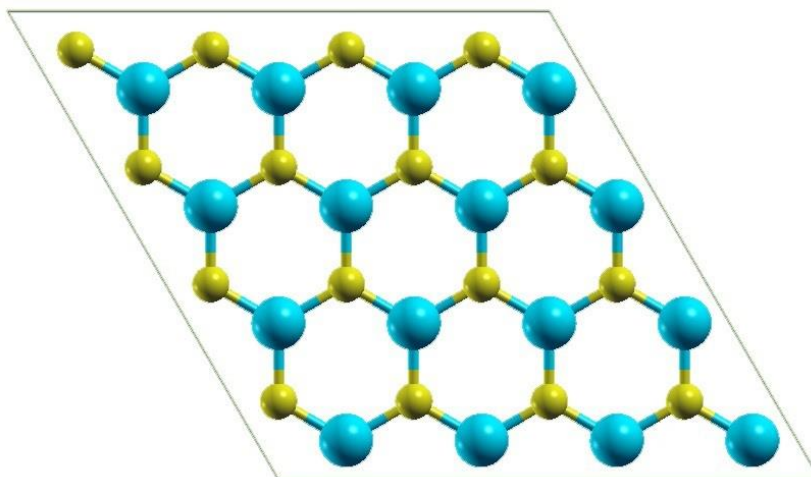


Fig. 1. Top view model of pure SiC sheet. Blue and yellow balls represent Si and C atoms, respectively.

In a previous theoretical calculation it is reported that the most stable structure of planar SiC forms graphene-like structure with alternative SiC bond and the bonding in such structure is of sp^2 type (Miyamoto, 2002). In our calculation we have considered similar structure and optimized without any symmetry constraint. In the optimized geometry, all the Si-C bonds are found to be identical. The calculated Si-C bond length of the sheet is about 1.7788 Å and the Si-C-Si angle is 120° which are in a good agreement with previous calculations and experimental reports (Lin et al, 2013), (Lin, 2012). In order to study the electronic and optical properties of the structure, the results of the band structure diagram is important, because we can derive the conductive properties of the structure out of it. The Band Structure of the silicon carbide nanosheet is shown in fig. 2. The results show that the considered structures band gap is about 2.5821 eV which indicates that it is a semiconductor with approximately large band gap. This result is very close to the reported band gap (Bekaroglu et al, 2010).

Table1: Bond length and cell parameters of the structure; before and after optimization.

	Before Optimization	After Optimization
Bond Length (Å)	1.78	1.7788
Cell Parameter (Bohr)		
a	23.30448380	23.28885553
c	1.21632781	1.21714439

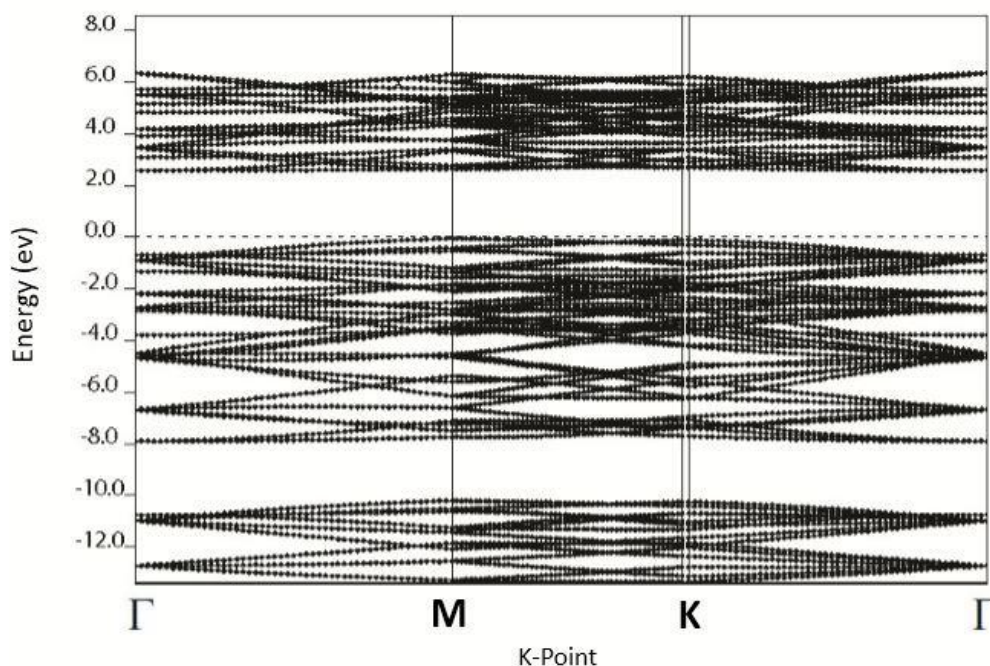


Fig. 2 : Band structure of the pure silicon carbide nano sheet.

After establishing the pure structure and studying the electronic properties of SiC nano sheet, we attempt to investigate this property of the nano sheet under hydrogen adsorption. To this end, four different types of hydrogen adsorption are considered: (1) adsorption of hydrogen atoms on silicon atoms, (2) adsorption of hydrogen atoms on carbon atoms, (3) adsorption of hydrogen atoms on silicon and carbon atoms at the two opposite sides of SiC sheet (4) adsorption of hydrogen atoms on silicon and carbon atoms at the same side of SiC sheet. It is vital to say that the first and second states were not converged so we assumed they were not stable states. As a result, we continued our work on the last two states. State (3) have had a total energy about -346.12 Ry, on the other hand, state (4) have had a total energy about -344.16 Ry. Therefore we picked state (3) as the most stable state for hydrogen adsorption; adsorption of hydrogen atoms on silicon and carbon atoms at the two opposite sides of SiC sheet.

The figures of these two states are shown below. (fig. 3)

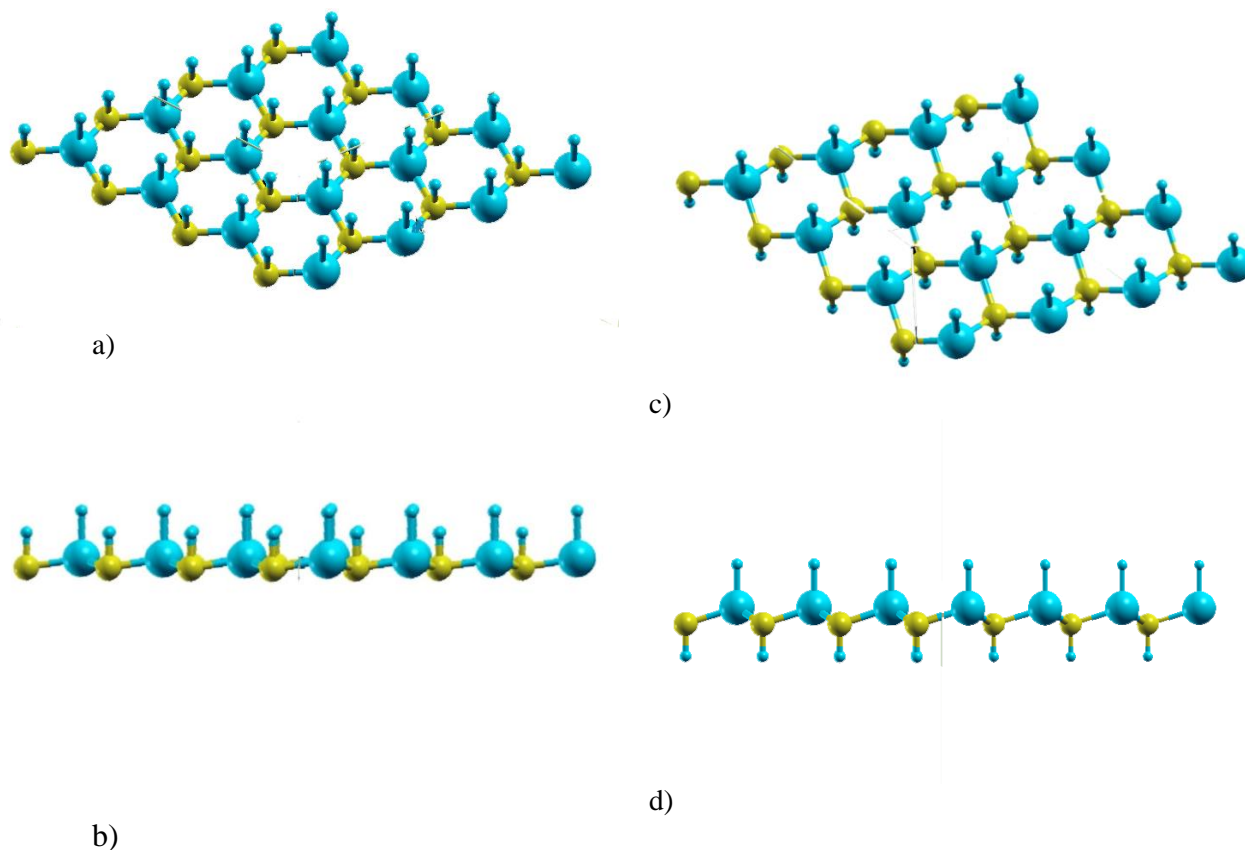


fig. 3: (a) Top view and (b) side view model of hydrogenated SiC nano sheet in state (4).
(c) Top view and (d) side view model of hydrogenated SiC nano sheet in state (3)
(Big blue and yellow balls represent Si and C atoms, respectively; little blue balls represent hydrogen atoms.)

Different states of hydrogen adsorptions on the SiC nano sheet are illustrated in Fig. 3. As we've said before, the two first states were not stable. As it is observed, different states of hydrogen adsorption are considered in this study: adsorption of hydrogen atoms on silicon and carbon atoms at the two opposite sides of the SiC sheet (state number three) and adsorption of hydrogen atoms on silicon and carbon atoms at the same side of the SiC sheet (state number four). It should be remarked that the relaxed structures are exactly shown in Fig. 3.

After establishing the hydrogenated structure, we have studied the electronic properties of the silicon carbide nano sheet under hydrogen adsorption. For this purpose, we again refer to the band structure diagram. This diagram is so important, because we can derive the conductive properties of the structure out of it.

The Band Structure of the silicon carbide nanosheet under hydrogen adsorption is shown in fig. 4. The results show that the considered structure's band gap is about 3.9499 eV which is much more than the pure silicon carbide nano sheet.

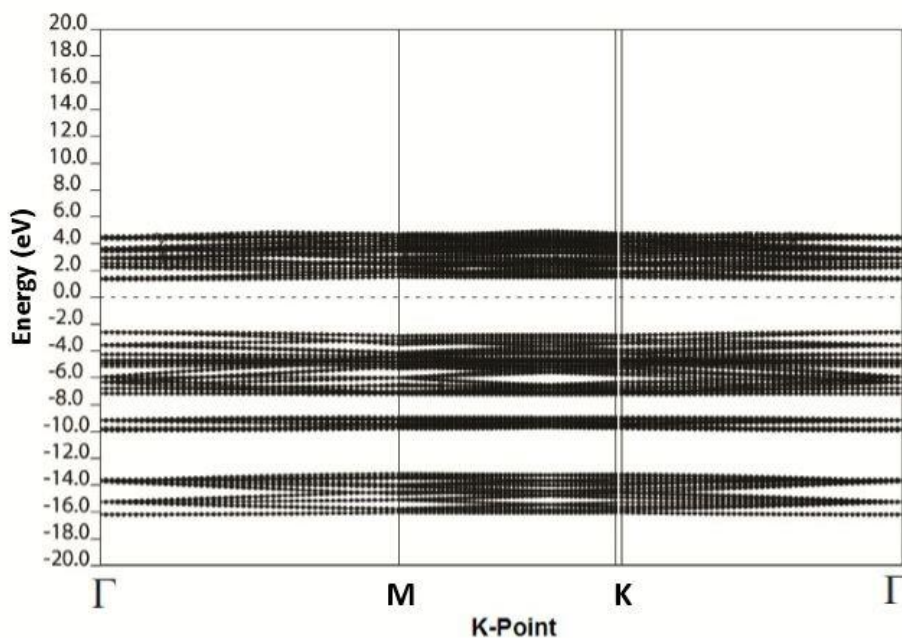


Fig. 4 : Band structure of the hydrogenated silicon carbide nano sheet.

Conclusion

In this study we've studied electronic properties of silicon carbide nanosheet under hydrogen adsorption based on the Density Functional Theory (DFT) and using Quantum Espresso simulation software. The results of these calculations have shown that the SiC nanosheet is a semiconductor with a band gap about 2.5821 eV. This material has high strength and is widely used in electronic devices. We've also tried different positions on the SiC nano sheet for hydrogen adsorption. After testing several positions, it was concluded that the most stable state happens when hydrogen atoms are adsorbed on silicon and carbon atoms at the two opposite sides of silicon carbide hexagonal nano sheet. The results have shown that this structure was the most stable one among those four, with a total energy about -346.12 Ry. Finally, we calculated the band gap of the hydrogenated SiC nanosheet, which is about 3.9499 eV.



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