On the existence of Si–C double bonded graphene-like layers

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1. Introduction

Silicon carbide is one of the hardest materials and is very suitable for electronic devices made for operations in extreme conditions, such as in high-power, high-frequency and high-temperature environments [1]. There is a wide spread interest in SiC materials for electronic and opto-electronic applications. Interestingly, though carbon and silicon have the same valence structures and diamond-type bulk SiC materials are available, graphene-like SiC has not been reported so far. In fact a key feature of graphene-like SiC materials, the Si=C double bonds, are yet to be found in extended or periodic SiC structures, whereas the C=C double bonds can be found easily [2]. This is mainly due to the large energy differences between their double bonds can be found easily [2]. This is mainly due to the large energy differences between their double bonds, whereas the C=C double bonds, are yet to be found in extended or periodic SiC structures, whereas the C=C double bonds can be found easily [2].

Recently, multi-walled SiCNTs have been successfully synthesized by different groups (for example, Refs. [6–11]). For example, using alumina membranes as templates, well aligned SiC tubular structures were prepared by Wang et al. [10] with tailored diameter and wall thickness. These tubes showed semiconducting behavior, as expected. In fact, SiCNTs were first synthesized by Sun et al. [6] via the disproportionate reaction of SiO with multi-walled CNTs. Multi-walled SiCNTs with no oxygen content were demonstrated by transmission electron microscopy. Interestingly, these SiCNTs exhibited much larger inter-layer distances (3.8 Å, 4.2 Å and 4.5 Å, etc.) than multi-walled CNTs (typically 3.4 Å). By analyzing their data from electron-energy-loss-spectroscopy (EELS), the authors also noted the possible π-like bonding between Si and C from these SiCNTs. If these results are theoretically justified, the difficult-to-make Si=C double bonds in an extended system may have indeed been demonstrated. Thus, this multi-wall SiCNTs may provide a pathway for future realization of SiC graphene-like materials.

In this Letter, we present DFT calculations to justify the existence of Si=C double bonds in the multi-walled SiCNTs, by understanding the origins of the peculiar large inter-layer distance found in the multi-walled SiCNTs. Our DFT–LDA calculations reveal that to exhibit the large interlayer distances, the walls of the nanotubes must be SiC monolayers. Such SiC monolayers are graphene-like and exhibit Si=C double bonds. They must also be arranged in a way so that Si (C) atoms in one layer are on the top of Si (C) atoms in the next layer. Otherwise, the SiC monolayers would buckle with strong interlayer interaction, leading to much smaller interlayer distances. We further found that the actual interlayer distances are determined by the Si/C ratios in the monolayers. Our calculated interlayer distances with various Si/C ratios agree well with the experimentally observed distances. Thus, our results provide strong justifications for the π-bonding feature observed by EELS.
in SiCNTs and suggest that Si–C double bonds in extended system may be realized in extended/periodic system such as in SiCNTs.

2. Computation methodology

Our calculation were carried out using LDA [12] to DFT and the projected augmented wave (PAW) basis [13] as implemented in the VASP 4.6.21 [14]. Generalized gradient approximation (GGA) has also been tested but it failed to find any minima for SiC bi-layer with Si-on-Si arrangements, consistent with the fact that LDA works much better than GGA for systems with weak interaction. Plane-wave cut-off energy of 400 eV was used, and the ion positions were always relaxed until the force on each of them was 0.01 eV/Å or less. Periodic supercell approximation with slab structure (with 2 layers or more) was used to calculate the inter-layer interactions. To minimize the periodic interaction between the slabs 25 Å vacuum layers has been added to the supercell. All the structures were fully relaxed.

We used supercells containing various number of SiC monolayers to model multi-walled SiCNTs with large tube diameters based on two main reasons. Firstly, it saves computing time tremendously as compared to modeling real multi-walled SiCNTs. Secondly, such modeling method for multi-walled SiCNTs with large tube diameters is justified by earlier DFT calculations [15–20]. For example, with self-interaction-corrected local LDA to DFT (LDA-SIC), Baumeier et al. [16] has calculated the electronic properties of SiCNTs with periodic supercells and found that the radial buckling diminishes quickly with the increase of the SiCNT’s diameter. For example, their smallest (4, 0) zigzag has a buckling of 0.230 Å, whereas the biggest tube (15, 15) armchair has a buckling of only 0.035 Å. With the finite cluster approximations, Alam and Ray [17] reported even less buckling for larger diameter tubes. Their largest diameter SiCNT (11, 11) has a buckling of only 0.009 Å. Baumeier et al. [16] and Zhao et al. [18] have also calculated strain energy for SiCNTs with both armchair and zigzag structures and showed that the strain energy reduces and saturates as the SiCNT diameters increase. This situation is similar to the boron nitride nanotubes [21]. These studies suggested that for the larger diameter SiCNTs smoother SiC hexagonal walls are possible due to lower strain energy, and the interlayer interaction in such multi-walled SiCNTs can be modeled by SiC layers in a supercell.

3. Results and discussion

We first discuss the electronic properties of a single graphene-like SiC sheet. We relaxed the cell without any symmetry constraint. We have intentionally induced buckling in the monolayer (both uniform and non-uniform buckling) before the relaxation. These buckled SiC monolayer always relaxed into a flat layer without any buckling. We also tried to cluster Si (C) atoms together, instead of alternate Si–C bonding, as this type of configuration is preferred in finite SiC clusters [22–24]. This type of Si–C segregation due to clustering is responsible for fact that SiC do not form high symmetric fullerene structures [25]. However, interestingly SiC alternate bonding was found to be favorable for the SiC monolayer. The band structure of the SiC monolayer is similar to that published in previous studies (for example in Ref. [16]). Obvious difference between the graphene and SiC graphene-like monolayer is that at a special point K in the Brillouin zone there is a band gap opening for SiC. We found the LDA band gap is direct and 2.554 eV. This band gap opening for SiC is due to its ionic feature, and the symmetry breaking between the two hexagonal sub-lattices (Si and C sub-lattices). The ionic feature between Si–C bonds arises from the difference in electronegativity of Si and C. Now, the Si–C bond length in SiC monolayer is 1.79 Å, much smaller than that in β-SiC bulk, 1.89 Å. With this bond length, π-bonding feature can be observable. In bis-silene [4] Si–C double bond-length was reported to be 1.77 Å, very close to SiC monolayer bond lengths. This is an indirect band gap of 1.710 eV is found for this bi-layer system. For the second stacking sequence as shown in Fig. 2b, a large interlayer distance of 4.138 Å is found. There is almost no buckling in each of the individual layers, indicating that each layers preserved their original bonding nature, the sp2 bonding. The band gap here is 1.855 eV, which is 0.699 eV lower than that of SiC monolayer. The first stacking sequence is about 0.234 eV/SiC-pair lower than the second stacking sequence, indicating that Si on Si configuration in stacking sequence 2 is a meta-stable state. We have tested up to 5 SiC monolayers in similar (Si on Si) stacking pattern. A minima interlayer distance of around 4.000 Å was always found. In contrast, for boron nitride graphene like sheet, the interlayer distance

![Fig. 1. Atom projected p-DOS for graphene-like SiC monolayer. VBM and CBM are clearly seen to be mainly composed of C-p and Si-p, respectively; and sp-hybridization has started at somewhat lower energy from the VBM. This implies that π-bonding between Si and C dominates the band-edges. Right upper hand corner showed the top and side view of the relaxed SiC monolayer.](image_url)
for two such layers were calculated to be 3.201 Å, which is very close to the h-BN interlayer distance of 3.33 Å[26].

In the case shown in Fig. 2c, one more SiC layer is added to the two monolayers arranged in Fig. 2a in the second stacking sequence. This gives a configuration of mixed stacking sequence. The bottom two layers are taken from the relaxed structure shown in Fig. 2a. After relaxation, the average distance between the third and the bi-layers is 3.880 Å. The inter-layer separation within the bi-layer is slightly smaller than that in the previous case without the third layer (Fig. 2b). The third layer remains flat without any buckling. The buckling in the bi-layer has very little impact on the third layer. For three SiC monolayers with stacking sequence (1) (Si on C), the inter-layer distance is increased to 2.242 Å. However, for 4 SiC monolayer arranged in stacking sequence (1) (Fig. 2d), strong sp3 bonding take place and the average interlayer distance falls to 1.986 Å. In Fig. 2e, we show two SiC bi-layers as in Fig. 2a on top of another in stacking sequence (2). Here the average inter-planar distance would become 4.005 Å. Interestingly, however, when we put two tri-layers together instead of two bi-layers, as shown in Fig. 2e, no large separation was found and C–C bonds are formed between the top and bottom tri-layers (Fig. 2f) with clear sp3 bonding, even though these two tri layers have the stacking sequence (2) between the facing layers. Similar results were found as the number of layers increased on outer two sides. So the large inter-layer distances can occur only between monolayers and bi-layers. For 4 or more monolayers with Si on Si stacking pattern, there are other local minima at shorter inter-layer distance with sp3 bonding. So if the layers are pushed to closer distances, the higher inter-layer separation would collapse. The higher separation of monolayers is only meta-stable for 4- or more SiC monolayers. To compare the relative stability of the SiC layer with respect to its bulk phase, we compare it with the SiC cubic structure. As expected, similar to C and BN, SiC bulk phase is more stable than the corresponding monolayer. It was found that the total energy of the bulk phase is 1.23 eV per Si–C pair more stable than the SiC mono-layer. This large energy difference is due to the strong preference of the Si–C pair to form sp3 bonding. This sp3 bonding preference would cause the collapse of SiC layers to form sp3 bonded layers. This also shows why most of the experimental SiC nanotubes had collapsed structures [7–11]. However, in Ref. [6] at higher inter-layer separation, the meta-stable phase did stabilize in the experimental environment. A 200 kV electron beam annealing for 5 min was needed to induce a collapse of these nanotubes with the minimal Si–C distance [6]. This clearly indicates an energy barrier between the collapsed and highly separated SiC layers.

We have further examined the dependence of interlayer distance on the Si/C ratios. With 4 × 4 × 1 super cell we have calculated SiC bi-layer separations for Si/C ratio of 1:31 and 2:30 with Si atoms always on top of Si atoms. The inter-layer distances were found in these two cases were 4.47 Å and 4.38 Å, respectively.
without any visible buckling. It is interesting to note that for graphene bi-layer the relaxed inter-layer distance is 3.6 Å, and for 1:1 SiC bi-layer the interlayer distance was found to be 4.138 Å. In these two extreme cases no buckling was seen. One might expect that by putting Si atoms in graphene bi-layer network (as in stacking sequence 2), the inter-layer distance would increase linearly until it reaches to 1:1 SiC bi-layer distance. Surprisingly, however, we found that substitution of one pair of Si atom on top of another in graphene bi-layer leads to a sudden increase in the interlayer distance (4.47 Å). This unexpected inter-layer distance trend can be explained as the following. When two Si atoms substitute two C atoms (on top of each other) in graphene bi-layer, there are positive charge accumulations on these substituted Si atoms, which induce strong Coulomb repulsion and pushes the two bi-layer away. When more C atoms are substituted by Si atoms, this charge accumulation was shared by all the substituted Si atoms, and the overall coulomb repulsion is reduced, and inter-layer separation decreased. On the other hand, for some intermediate ratios of Si/C, such as 3:29, 4:28, and up to 10:22, the two SiC bi-layers can form interlayer bonding. For example, for a ratio of 3:29, the carbon atoms surrounded by three Si atoms formed bond with the carbon atom below it from the bottom layer. In these cases, the surrounding Si atoms formed sp3-type bonding, as seen in the Fig. 3, and the overall inter-layer distance (away from the bonding area) increased to 5 Å or more. In all these cases buckling has been found. However, as the Si atoms content increases in the SiC layer, both the inter-layer bonding and buckling were eventually vanished.

We now compare our calculated results with the experimentally observed interlayer distances. The reported interlayer distance were large, (3.8 Å, 4.2 Å and 4.5 Å, etc.). No inter-layer separation below or around 2.5 Å was reported for un-collapsed SiCNT [6]. It is interesting to note that the interlayer distances of SiCNTs (for example, 4.3 Å) increased from that of CNT’s (3.4 Å) almost by a factor of the bond length ratios of Si–C and C–C in the respective nanotubes (1.79/1.43). However, this could be quite coincidental. As the distance between the layers are large, so the higher distance in SiC layers could be only due to the long range Coulomb interaction resulting from the charge segregation in the Si and C, compared to only C in MWCNTs. Based on our DFT results, the observed large interlayer distances suggest strongly that the experimentally observed SiCNT systems must be Si–C monolayer with stacking sequence (2), i.e., Si (C) atoms of one monolayer are on the top of Si (C) atoms in the next monolayer. These SiC monolayers have no buckling and present sp2 bonding at near 1:1 Si:C ratio. In these 2-D periodic cases, as explained above, sp2 double bonding, Si=C, is the possible bonding structure. The interlayer distance trend can be explained by the Si:C ratio variation in the SiC monolayers. Our calculations reveal that larger distances was are due to less Si content in the layers. Such Si:C ratio variation is expected in the reported SiCNTs [6], because SiNTs were formed by diffusing Si atoms into CNTs.

4. Conclusions

In conclusion, we have established that Si–C double bond has been found in periodic SiC graphene-like multi-layer systems. We have found that SiC monolayer favors sp2-type bonding and its’ Si=C double bond length is very close to the experimentally found double bond-length of bis-silene. We have shown that the large interlayer distances found in multi-wall SiCNTs in a previous experiment [6] can only be understood by the arrangement of Si=C double bond containing SiC monolayers in a special stacking sequence. Otherwise, a collapse of the SiC layers is highly possible which would results in the tetrahedrally bonded SiC layers, as is obtained in many other experimental studies. The variable distance of these Si=C double bonded layers depend on the ratio of Si and C atoms. Our results justify that the π-bonding feature observed by EELS in SiCNTs and suggest that graphene-like SiC layers can exist.

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References


Fig. 3. SiC bi-layer with 3:29 ratio. Three orange Si atoms provided sp3 environment to facilitate the C–C bonding. For some of the intermediate ratios of Si:C this bi-layer bonding takes place. The inter-layer distances in these cases are larger than 5.00 Å. As these distances were not observed in the experiment [5], these types of sp3 Si–C bonded systems can be ruled out for SiCNT formation. However, this inter-layer C–C bonding eventually vanished when the number of Si atoms increased in the SiC-layer.