

## A FIRST PRINCIPLE CALCULATION OF SILICENE AND GRAPHENE USING QUANTUM ESPRESSO SIMULATOR

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### ABSTRACT

We use first-principles density functional theory based calculations to determine the energetics of graphene and properties of silicene, a graphene-like structure made from silicon, and explore possibilities of modifying its structure and properties to determine the likeness and dissimilarities between graphene. Our calculations are based on the generalised gradient approximation of the Perdew-Burke-Ernzerhof (GGA-PBE). Our results shown that using quantum espresso that graphene (carbon) is more stable compare to silicene evident from both the value of the minimum energy and cohesive energy, and that while pure silicene is stable in a distorted honeycomb lattice structure obtained by opposite out-of-plane displacements of the two Si sub-lattices, its electronic structure still exhibits linear dispersion with the Dirac-conical feature similar to graphene.

**Keywords:** Silicene, graphene, minimum and cohesive energy

### 1. INTRODUCTION

Graphene, a two-dimensional honeycomb lattice of  $sp^2$ -bonded carbon atoms, has attracted an intense research activity (Geim and Novoselov, 2007). As a result of its unique electronic structure that exhibits high linear dispersion at a high symmetry point in the reciprocal space, leading to electronic dynamics similar to that of massless relativistic Dirac fermions (Novoselov *et al.*, 2005). Recently, there has been evidence from experiment on the formation of silicene on silver substrate, showing that the choice of substrate may help in stabilizing silicene and related structures (Kara *et al.*, 2009). It is expedient to explore other possibilities of silicon, an element close to carbon in the periodic table, to see whether it would exhibit a similar structural form and properties, while carbon is known to occur in the form of cage-like clusters, such as fullerene (Dresselhaus *et al.*, 1996) or carbon nano-tubes. Similar structures of silicon are known to be stable only with metal atoms placed inside the cage or the tube, called as endohedral clusters or tubes (Kumar, 2007). The option of stabilizing structures through endohedral encapsulation of metal ions is not possible with a two-dimensional honeycomb lattice. However, it is known that silicon forms three-dimensional crystals with certain metals, such as Ti, Nb, Ta, Cr, Mo and W (Jianguang *et al.*, 2003). One of the crystallographic planes of these silicides, relevant to their dislocation activity (Waghmare *et al.*, 1999), consists of a honeycomb lattice of silicon atoms with a metal atom located at the centre of each hexagonal ring. In this work, we present some interesting properties of carbon, silicene and their electronic properties. This paper is organised as follows: In Section 2, the computational methodology is presented followed by result and discussion in Section 3, and finally In Section 4 the conclusion is presented.

## 2. COMPUTATIONAL METHODOLOGY:

We used the quantum espresso (Baroni *et al.*, 2009) implementation of first principle density functional theory (DFT) with PW91 functional of the generalized gradient approximation (GGA) (Perdew and Wang, 1992) for the exchange correlation energy of electrons. In DFT method, the core electrons are usually separated from the valence electrons. We used ultra-soft pseudo-potentials (Vanderbilt, 1990) to represent the potential of the nuclei and core electrons of atoms, and a plane-wave basis with an energy cut-off of 30 Ryd to represent Kohn–Sham wave functions, k\_points of 20 20 1 0 0 0 was maintained for all calculations. Throughout this process, the lattice constant was varied from the input file from 7.67 to 8.02(Bohr) for which corresponding total energy was generated and stored. By using xmgrace a graph of total energy vs lattice constant was plotted and the phonon calculation was carried out. The phonon frequency generated shows that the structure is unstable. Then the structure was then distorted (relax) to get even lower energy state, the bulk modulus was also calculated using fitted equation. This process was repeated for carbon (graphene). Phonon dispersion along the high symmetry lines in the Brillouin zone was obtained using Fourier interpolation from a  $2 \times 2 \times 2$  mesh of k-points. For pure silicene, the frequencies of phonons at other wave-vectors in the Brillouin zone were determined to assess the overall stability also for carbon.

## 3. RESULTS AND DISCUSSION:

### 3.1 SILICENE

The lattice constant of silicene corresponding to the minimum total energy ( $E_{\min}$ ) is 7.34(Bohr). While the  $E_{\min}$  was found to be -19.12 Ry, the phonon frequencies for the final stable structure of silicene are given as 263, 504, 504. The bulk modulus was also calculated using fitted equation, and we obtained  $72.10 \text{ J/m}^2$ , the bond length of Si-Si was 2.29Å. Table 1 shows the calculated physical properties of silicene and the plotted electronic band structure is displayed by Figure 1(b)

### 3.2 CARBON (GRAPHENE)

All the procedures adopted for silicene was repeated for carbon (graphene) with the following results: the lattice constant was 4.67(Bohr), graphene was found to be stable with minimum energy  $E_{\min} = -22.83 \text{ Ry}$ , phonon frequencies for the stable graphene structure were 878, 1550, 155. The bulk modulus was also calculated using fitted equation (total energy vs area) the value of the Bulk modulus was  $220 \text{ J/m}^2$ . The calculated bond length was 2.7bohr showing strong bonding, while the cohesive energy is 9.09(8.97) for carbon (graphene). Electronic band structure was also plotted, Table 2 shows structure, energetics, elastic and point vibrational properties of graphene. Cohesive energies in parenthesis are for the diamond structure.

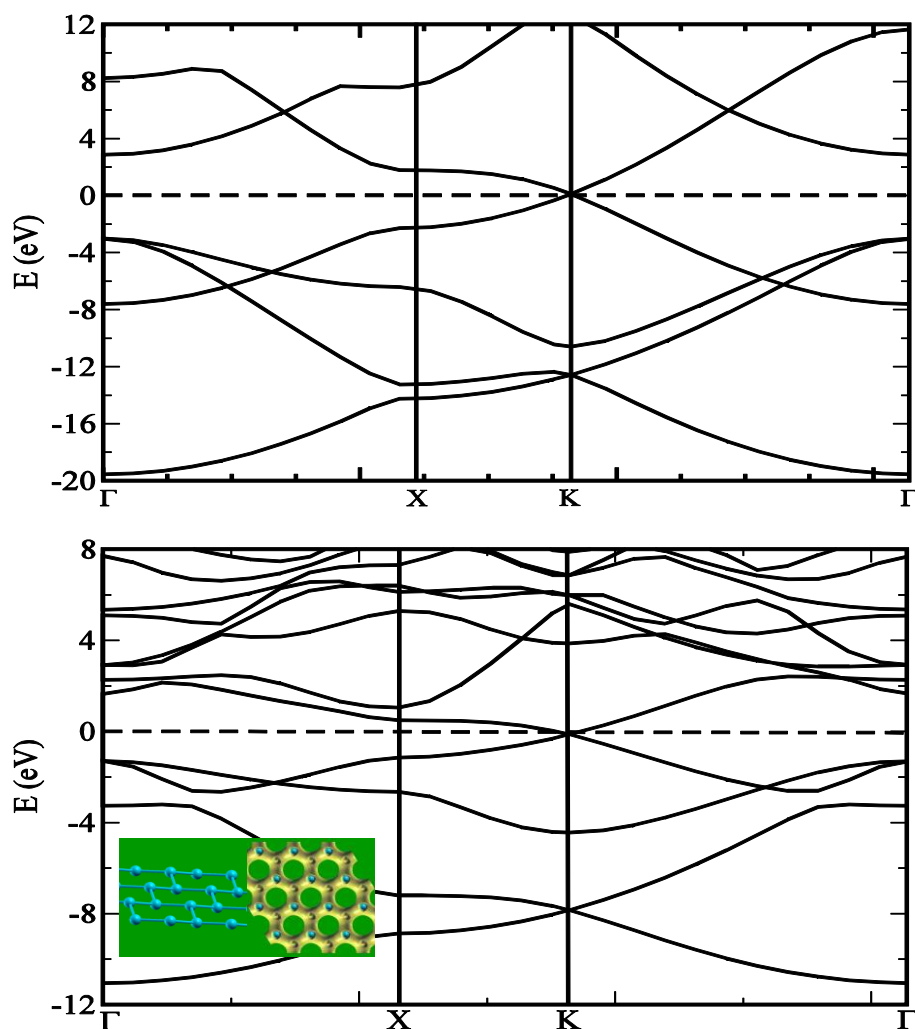


Fig. 1. Electronic structure of graphene (a) and silicene (b). The distorted honeycomb structure of silicene and an iso-surface of its electronic density is shown in the inset of (b).

Table 1. Structure, elastic energetics and  $\gamma$ -point vibrational properties of silicene

Properties	Silicene
Lattice constant (bohr)	7.34
Calculated bond length (bohr)	4.24
Bulk modulus ( $\text{Jm}^{-2}$ )	72
Cohesive energy (eV/atom)	4.70 (5.30)
Phonon frequencies ( $\text{cm}^{-1}$ )	263,504,504

Table 2. Structure, energetics, elastic and  $\gamma$ -point vibrational properties of graphene..

Properties	Carbon Graphene)
Lattice constant (bohr)	4.67
Calculated bond length (bohr)	2.7
Bulk modulus ( $\text{Jm}^{-2}$ )	220
Cohesive energy (eV/atom)	9.09 (8.97)
Phonon frequencies ( $\text{cm}^{-1}$ )	878,1550,1550

Cohesive energies in parenthesis are for the diamond structure

Table 3. Structure, energetics, elastic and gamma-point vibrational properties of graphene and silicene

Properties	Silicene	Carbon Graphene)
Lattice constant (bohr)	7.34	4.67
Calculated bond length (bohr)	4.24	2.7
Bulk modulus ( $\text{Jm}^{-2}$ )	72	220
Cohesive energy (eV/atom)	4.70 (5.30)	9.09 (8.97)
Phonon frequencies ( $\text{cm}^{-1}$ )	263, 504, 504	878,1550,1550

Cohesive energies in parenthesis are for the diamond structure.

### 3.3 STABILITY AND ELECTRONIC STRUCTURE OF SILICENE AND CARBON

For the planar structure of silicene, the energy was optimized, the calculation of the point phonons showed that this planar structure of silicene is unstable with respect to a mode in which silicon atoms on the two sub-lattices move in opposite directions perpendicular to the plane. The structural relaxation of the structure obtained by distorting a perfectly planar structure with this mode results in a stable structure (see Table 1) with a Si–Si bond length of 2.29 Å (note that the Si–Si bond length in the diamond structure is 2.34 Å). It is 0.02 eV/atom lower in energy than the planar structure. In this structure, the Si–Si–Si bond angle is  $115.6^\circ$ , reflecting a deviation from the perfect honeycomb structure. The bulk modulus of silicene (defined as  $B = A \frac{d^2E}{dA^2} \big|_{A_{\min}}$ , where  $A$  is the area of the periodic cell of the 2D lattice and  $A_{\min}$  is the area with minimum energy) is smaller than graphene by almost a factor 3.4, suggesting a much weaker bonds in silicene. The implication of this is that silicene would not be of much use in applications of materials requiring strong mechanically behaviour compared to carbon (graphene). The stiffness of the bonds is also reflected in phonon frequencies which are smaller by a factor of about three in silicene. Finally, the cohesive energy of silicene is about half of that of graphene, consistent with the relatively greater abundance of graphene than of silicene. We note that the cohesive energy of silicon in the diamond structure is larger and greater in stability than that of its graphene-like structure, while this is reversed for carbon, as expected.

As opposed to carbon, which is known to have  $sp^2$  hybridization favouring a planar honeycomb lattice, the forms of silicon are not known commonly to have bonding based on  $sp^2$  hybridization. Thus, the stability of silicene with a ‘buckled out-of-plane’ honeycomb lattice needs to be explored further. The thermal stability of graphene has been obtained using Molecular dynamics (Fasolino et al., 2007)), which showed that ripples on the scale of 7.9 nm form spontaneously in graphene at room temperature (RT) due to thermal fluctuations. As the phonon frequencies of silicene are much smaller than those of graphene, similar ripples are expected in silicene at lower temperatures. At low temperatures, classical molecular dynamics or Monte Carlo simulations are in no way applicable, as they correspond to Maxwell–Boltzmann statistics, while the statistics of phonon population follows the Bose–Einstein distribution. While detailed finite temperature simulations would, with respect to the lattice constant (or bond length). From the result obtained above for both silicene and carbon, the following conclusion can be made. Graphene (carbon) is more stable compared to silicene evident from both the value of the minimum energy and cohesive energy.

### 4. SUMMARY

The energy scale of the flexural modes in graphene is larger than that of silicene, showing that silicene is thermally much more unstable (with respect to formation of ripples) than graphene. Many unoccupied electronic bands in silicene suggest that it is expected to be sensitive to its external surrounding, which means significant changes in the structure due to

the details of substrate (as seen in the experiments of Kara et al. (2009)). In summary, we have carried out a systematic first- principles theoretical analysis of silicene and carbon. We showed that silicene in its pure form exhibits a distortion of the honeycomb lattice, yet an interesting electronic structure with a linear dispersion similar to that of massless Dirac fermions in graphene, but with a less energy scale.. Our results should give an insight in order to motivate experimental efforts to synthesize some of these systems, for the exploration of fundamental science as well as for applications in the industries and laboratories.

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## REFERENCES

- Baroni, S., Dal Corso, A., de Gironcoli, S., Giannozzi, P., Cavazzoni, C., Ballabio, G., Scandolo, S., Chiarotti, G., Focher, P., Pasquarello, A., Laasonen, K., Trave, A., Car R., Marzari, N. and Kokalj, A. (2009). QUANTUM ESPRESSO: a modular and open-source software project for quantum simulations of materials. *Journal of physics: Condensed matter* 21(39): 395-502.
- Dresselhaus, M.S., Dresselhaus, G and Eklund, P.C. (1996). "Science of Fullerenes and Carbon Nano-tubes: Their Properties and Applications", by Academic Press
- Fasasolino, Annalisa, J. H. Los, and Mikhail I. Katsnelson. "Intrinsic ripples in graphene." arXiv preprint arXiv:0704.1793 (2007).
- Geim, A.K. and Novoselov, K.S. (2007). "The rise of graphene, *Nature Materials* 6: 183 - 191
- Jianguang, X., Baolin, Z., Wenlan, L., Hanrui, Z. and Guojian, J. (2003). Synthesis of pure molybdenum disilicide by the "chemical oven self-propagating combustion method, *Ceramics International*, 29(5): 543-546.
- Kara, A., Léandri, C., Dávila, M.E., De Padova, P., Ealet, B., Oughaddou, H., Aufray, B. and Le Lay, G. (2009). Physics of silicene stripes. *Journal of superconductivity and novel magnetism* 22 (3): 259-263.
- "Nanosilicon", edited by Vijay Kumar (2007). Elsevier Science
- Novoselov, K.S., Geim, A.K., Morozov, S.V., Jiang, D., Katsnelson, M.I., Grigorieva, I.V., Dubonos, S.V. and Firsov, A.A. (2005). Two-dimensional gas of massless Dirac fermions in graphene". *Nature* 438: 197.
- Perdew, John P., Kieron Burke, and Matthias Ernzerhof (1996). Generalized gradient approximation made simple. *Physical review letters* 77.18: 3865.
- Vanderbilt, David. (1990) "Soft self-consistent pseudopotentials in a generalized eigenvalue formalism." *Physical Review B* 41.11: 7892.
- Waghmare, U.V., Kaxiras, E., Bulatov, V. and Duesbery, M.S. (1999).  $\langle 331 \rangle$  slip on  $\{013\}$  planes in molybdenum disilicide. *Philosophical Magazine* 79 (3): 655-663