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A Theoretical Study of Lattice Dynamical Properties of Silicene by DFT

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Silicene is a two-dimensional (2D) material showing high promises for nanoelectronics and thermoelectric applications due to its quantum spin Hall effect and tuneable band gap. However, a complete theoretical understanding of its fundamental properties like lattice dynamical properties and its comparison with graphene has remained elusive. This paper investigates the lattice dynamics, density of states (DOS), and band structure of silicene. The calculations show that the buckled structure of silicene couples the out-of-plane flexural vibrations with small in-plane components breaking the planar symmetry existing in graphene. Due to weaker interatomic bonds, the acoustic-phonon branches are less dispersive reducing the group velocities. We have used local density approximation (LDA) for density functional theory (DFT) based calculations to determine the properties of silicene, a graphene-like structure made of silicon. We have performed the structural optimization and calculated the DOS, band structure as well as phonon dispersion of silicene, a 2D-material. We have also compared the results for silicene with those for graphene. These results may provide some insights into this relatively new material. This may also initiate further interest in the exploration of fundamental science as well as for applications in industries and laboratories.

Силіцен — це двовимірний матеріал, який має високі перспективи для наноелектроніки та термоелектричних застосувань завдяки квантовому спіновому Голловому ефекту та ширині забороненої зони, що настраюється. Однак повне теоретичне розуміння його фундаментальних властивостей, таких як динамічні властивості ґратниці, та його порівняння з графеном залишаються недосяжними. У цій статті досліджуються динаміка ґратниці, густина станів і зонна структура силіцену. Розрахунки показують, що вигнута структура силіцену пов'язує позаплощинні вигинальні коливання з малими площинними компонентами, які порушують планарну симетрію, що існує в графені. Через ослаблення міжатомових зв'язків акустичні фононні гілки є менш диспер-

сійними, що зменшує групові швидкості. Ми використали наближення локальної густини для розрахунків на основі теорії функціоналу густини, щоб визначити властивості силіцену — графеноподібної структури, виготовленої з Силіцію. Ми виконали структурну оптимізацію та розрахували густину станів, зонну структуру, а також дисперсію фононів силіцену — двовимірного матеріалу. Ми також порівняли результати стосовно силіцену з результатами для графену. Ці результати можуть дати деяке уявлення про цей відносно новий матеріал. Це також може викликати подальший інтерес до досліджень фундаментальної науки, а також до його застосування в промисловості та лабораторіях.

Key words: silicene, density of states, band structure, phonon dispersion, density functional theory.

Ключові слова: силіцен, густина станів, зонна структура, дисперсія фононів, теорія функціоналу густини.

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1. INTRODUCTION

Silicene is a two-dimensional (2D) allotrope of silicon introduced by Guzmán-Verri and Lew Yan Voon [1]. 2D-materials are very interesting in their own right from the point of view of basic physics, as well as in technology. The recent progress in the characterization, growth, and understanding of the physical properties of graphene has paved the way for the study of other two-dimensional materials. Many layered materials have strong in-plane chemical bonds but relatively weak coupling between the layers and these layered structures can be cleaved into individual freestanding atomic layers. These layers with one dimension (1D) strictly restricted to a single layer are known as two-dimensional materials. Most of the inorganic materials have the quantum effect, which plays a key role in controlling the optical and electronic properties and such materials, both heat and charge transport are confined to a plane. However, in nanostructure, the ratio of high surface to volume also significantly affects the mechanical and chemical response. The two-dimensional materials all-surface nature offers the opportunity to tune its properties by surface treatments and it is called chemical functionalization. It is also interesting that, being just one-atom thick, two-dimensional materials immediately appear as the most suitable candidate to create, eventually, a new generation of electronic devices. According to Moore's law, two-dimensional materials with few atomic layers in thickness are favourable over bulk materials in terms of device scalability [2].

Silicene is a monolayer of hexagonally arranged silicon (Si) atoms

[3] and has been experimentally synthesized [4–10] and theoretically predicted [11–15]. Freestanding silicene exhibits essentially the same electronic properties according to DFT (density functional theory) calculations similar to its graphene counterpart [16]. 2D-silicene has recently been synthesized on Ag [17–19], Ir [20], Au [21], and ZrB₂ [22] substrates and has potential applications for electronic devices because it has unique physical and electronic properties similar to graphene. However, some issues have restricted the development of 2D-material silicene electronics, especially the absence of a band gap in the electronic structure of silicene [23–25]. The band gap of silicene can also be tuned by substrate [26, 27]. Additionally, silicene nanoribbons offer the possibility to achieve tuneable band structures due to the size effect. Previously some literature has reported that hydrogenation of silicene is an effective method to tune the band gap of silicene [28–30]. Silicene is believed to have a great future and the relevant studies are booming development for future research. In this paper, we have performed a DFT-based study on the electronic structure and phonon dispersion of the 2D-silicene.

2. COMPUTATIONAL DETAILS

All the calculations have been carried out within the DFT formalism [31]. We have used the local density approximation (LDA) [32] to treat the exchange–correlation functional with a double zeta (DZ) basis set as implemented in the Quantum ESPRESSO software [33]. Quantum ESPRESSO is an abbreviation for Quantum open-source Package for Research in Electronic Structure, Optimization, and Simulation, and it is more efficient for large clusters and extended systems [34]. The strength of LDA is that the errors in the exchange and correlation energy terms tend to compensate for each other. It generally provides a good description of bonding with a slight overestimation.

3. RESULT AND DISCUSSION

To obtain the optimized configuration of silicene, the unit cells of the considered single layer were relaxed in the axial direction until the stress components were less than 1 GPa. The optimization of atomic positions was allowed to proceed without any symmetry constraints until the forces acting on each atom were less than 0.02 eV/Å. After geometry optimization, the energy of formation was obtained to be −9.86 eV.

Figure 1 displays the optimized structure of the silicene in dif-

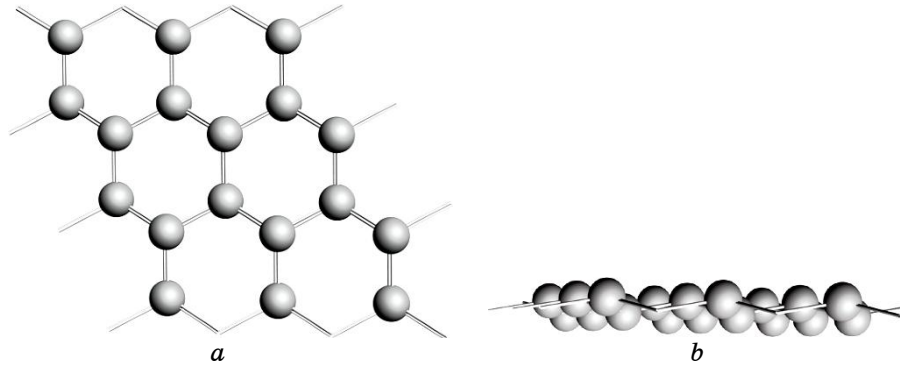


Fig. 1. Optimized geometry of 2D-silicene: (a) front view, (b) side view.

ferent views and the structural and electronic properties have been examined in detail. Unlike graphene, the structure of silicene is quasi-planar, which can be expected due to the difference in the nature of bonding of Si and C. For instance, Si fails to form the sp^2 hybrid double bond. In the optimized geometry of silicene (Fig. 1), bond shapes formed between silicon (Si) atoms are edge-stacking patterns and the value is due to the stacking of layers through edges that can modify the electronic properties of silicene. The zigzag structure supports localized states [35, 36] and results in covalent bond formation, anti-bonding, and bonding states. The local density approximation method underestimates the bond length and over-bind, which causes a more significant interatomic-force constant to be generated [37].

The electronic band structure of silicene is computed within LDA approximation based on DFT along the high symmetry point of the first Brillouin zone. The band structure explains the energy range an electron within the materials may have. The band structure of silicene is displayed in Fig. 2. One can see that a black coloured horizontal line divides into half the lower part called the valence band, and the other half the upper part, which is the conduction band. The minimum amount of energy required for an electron to jump across is the energy band gap (E_{gap}). The calculated E_{gap} of silicene is of 1.50 eV, which is greater than the graphene [38]. From the previous study, it has been clear that the two-dimensional silicene shows many similarities with graphene [39], in particular, the gap is also closing at the K -point of the Brillouin zone, and the dispersion around this point is linear. In contrast, two-dimensional silicene is quantitatively different from the 2D-graphene in which a conduction band is partially filled by electrons around the point, and therefore, the bands at the K -point are shifted up in energy, so that 2D-silicene is not a zero-gap material.

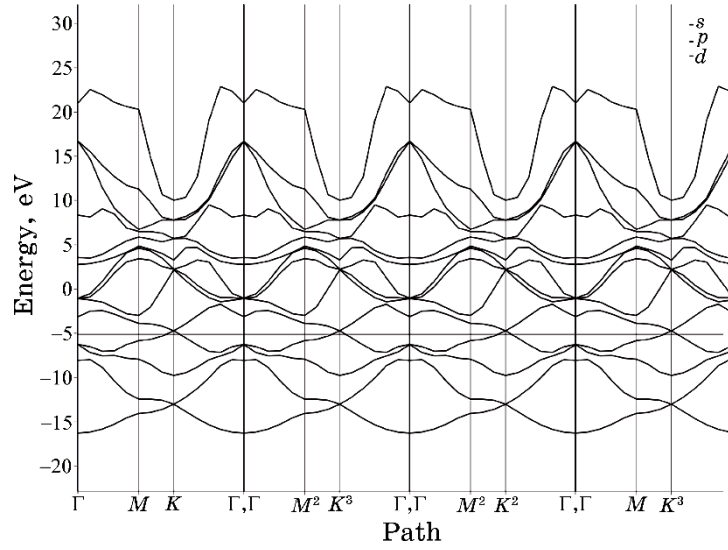


Fig. 2. Band structure of 2D-silicene.

The density of states (DOS) has also been calculated to explain the features of the band structure of silicene. The DOS represents the number of electron states per unit volume per unit energy and the present study type of calculation used was non-SCF. The DOS curve shows that overlapping population in the conduction/valence bands. The distribution of DOS for silicene structures is shown in Fig. 3. The DOS curve indicates that the population of valence and conduction bands of silicene is shifted upwards and downwards resulting in an E_{gap} of 1.50 eV. For the DOS curve, the Dirac point of the silicene where the DOS is zero is visible. From Figure 2, it is also clear that the DOS of silicene increases linearly with energy. For silicene, the Fermi energy is found to be coinciding with the valence band at -5.09 eV, which is higher than those are in the case of graphene structure, *i.e.*, -5.45 eV [40].

Phonons are considered as vibrational energy carriers. In a lattice with a basis of two atoms in the primitive cell, as in silicene, the allowed frequencies of propagation wave are split into a lower branch called the acoustical branch and an upper branch known as the optical branch. Acoustic phonons have wavelengths that become longer at small frequencies and correspond to sound waves in the lattice. Optical phonons have some minimum non-zero frequency of vibration, even when their wavelength is large. The phonon dispersion is the relationship between the phonon wave-vector $\mathbf{q}$ and its energy E . In this section, we describe the LDA-calculated phonon dispersion curve of silicene.

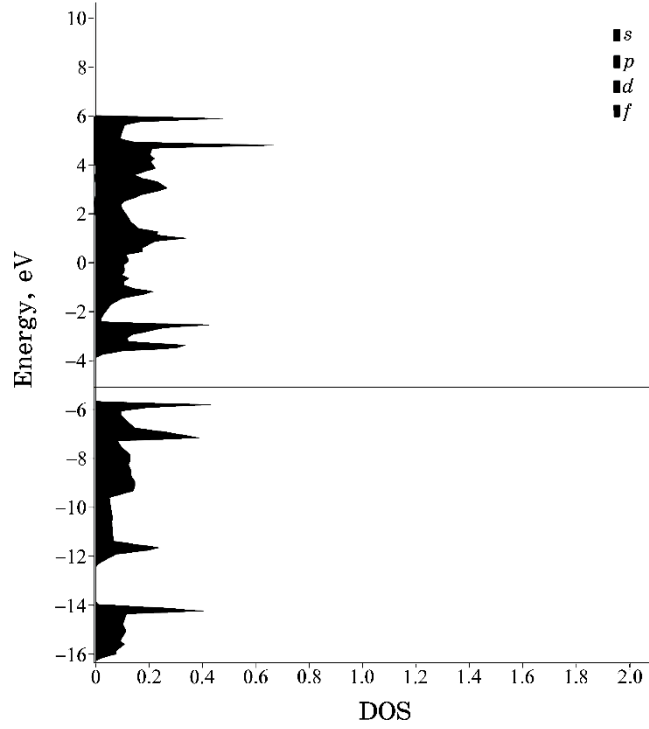


Fig. 3. The density of states (DOS) of *2D*-silicene.

The calculated phonon dispersion curves of *2D*-silicene along high symmetry lines within the Brillouin zone are shown in Fig. 4. The dispersion lines are similar due to their similar honeycombed lattice structures. Graphene has mirror symmetry about the atomic plane, such that the atomic motions along the *Z*-direction are decoupled from those in the *X*-*Y* plane in the harmonic approximation. The acoustic and optical modes along the *Z* direction do not couple with other phonon modes, resulting in crossings of dispersion lines in graphene [41]. For silicene, the slight buckling of the atoms in the *Z*-direction breaks the mirror symmetry and the hybridization becomes stronger for larger buckling. Thus, the phonon dispersion curves of silicene have some unique features.

4. CONCLUSIONS

To conclude, we have reported a systematic DFT-based study on *2D*-silicene using the LDA approach as implemented in the open-source Quantum ESPRESSO software package. These results showed that silicene in its pure form exhibits a distortion of the honeycomb lat-

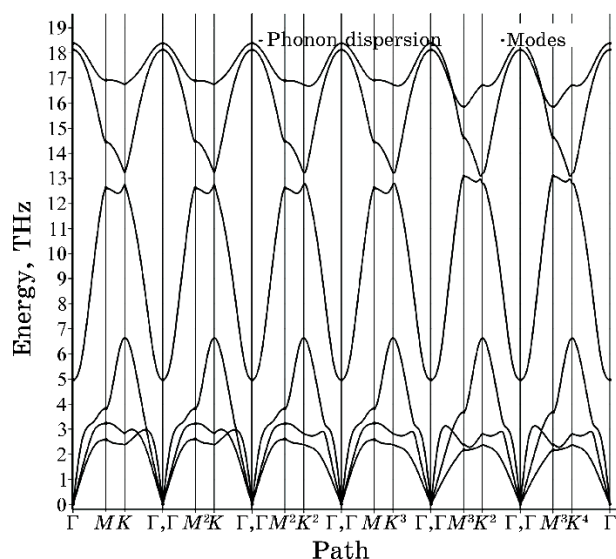


Fig. 4. Phonon dispersion curves of 2D-silicene.

tice, yet an interesting electronic structure with a linear dispersion but with a less energy scale. Despite being a close analogue of graphene, it has several unique features. These theoretical results may be useful for applications in industries and laboratories as well as for the exploration of basic science of 2D-materials.

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