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Synthesis of new silicene structure and its energy band properties

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Abstract

Silicene, silicon analogue to graphene possesses a two-dimensional (2D) hexagonal lattice, has attracted increasing attention in the last few years due to predicted unique properties. However, silicon naturally adopts the three-dimensional diamond structure, so there seem to be not any natural solid phase of silicon similar to graphite. Here we report the synthesis of new silicene structure with a unique rectangular lattice through using irradiation of coherent electron beam on amorphous silicon nanofilm produced by pulsed laser deposition (PLD). Under coherent electron beam irradiation with proper kinetic energy, the surface layer of silicon nanofilm can be crystallized into silicene. The dynamic stability and the energy band properties of this new silicene structure were investigated using first-principle calculations and density function theory (DFT) with the observed crystalline structure and lattice constant, which has a real direct bandgap of 0.78eV. It is interesting in the simulating calculation that the convex bond angle with 118° was measured in the new silicene structure with rectangular lattice. The DFT simulations reveal that this new silicene structure has a Dirac-cone like energy band. The experimental realization of silicene and the theoretically predicted properties shed a light to silicon material with potential new device applications.

Keywords: Silicene, nanofilm, irradiation of coherent electron beam, pulsed laser deposition, Dirac-cone

PACS: 42.55.–f, 68.65.Hb, 78.45.+h

Graphene has grabbed the worldwide attention since the first experimental preparation reported in 2004 owing to its fascinating properties and many device applications, such as K.S.Novoselov, et al. discovered the Electric field effect in thin carbon films and the two-dimensional gas of massless Dirac fermions in grapheme [1, 2], Kim (2009) investigated on growth of graphene films for stretchable transparent electrodes [3] and Seol studied on phonon transport in supported grapheme in 2010 [4]. Since then, two-dimensional (2D) materials have gained rapid development. In last few years, B.Feng and B.Lalmi, et al. (2010~2012) have invested strong effort to growth of 2D silicon material [5, 6], which was expected to have a great impact on the development of future electronic devices and energy storage [7-9]. The 2D silicon material was named either analogue of graphene in K.Takeda's work (1994) or silicene in G.G.Guzmán-Verri's work (2007) [10, 11]. Recent related theoretical work contributed by W.F.Tsai, G.A.Tritsaris and L.Tao, et al. (2012~2015) revealed that the silicene has a structure of Si atoms packed in a buckled honeycomb lattice, and it possesses massless Dirac fermions and other attractive properties [12-14], in which C.-C.Liu, P.Vogt and Jiajun Linghu, et al. (2011~2017) have invested stronger effort [15-17]. However, the valence electrons in silicon are localized in σ bonds and less mobile than those in graphite, in which Y.Yamada-Takamura and R.Friedlein (2015) indicated that it prevents the formation of extended π electronic states at low binding energies [18]. Therefore, the silicon crystal naturally adopts the three-dimensional diamond structure and so no natural solid phase of 2D silicon crystal. The silicene really belongs to the kind of quasi-2D silicon crystal. Typically, C.L.Lin, H.Jamgotchian and E.Scalise, *et al.* prepared silicene by depositing silicon on metal substrates [19-21]. Other structures such as silicene nanoribbons have also been prepared on Ag (110), in which graphene-like electronic signature was observed by B.Aufray and P.De Padova, *et al.* (2010) [22, 23]. The electronic properties of silicene grown on Ag (111) were also investigated by D.Chiappe, et al. (2012) [24]. Although silicene has been demonstrated for unique properties, their synthesis on silicon directly is still difficult for available, the realization of such structure would be able to fully explore its potential.

In other ways, T.Morishita and K.Nishio, et al. used molecular dynamics simulation to study the formation of nanowire and double-layer silicon in slit pores [25, 26]. Their stability is further confirmed by first principles calculation. The calculations demonstrated the possibility of the synthesis of novel nanosilicon by confinement in nanopores. And J.Bai, *et al.*(2010) suggested that the bilayer hexagonal silicon is a quasi-2D semimetal in the double-layer silicon computation [27]. It is interesting to make a comparison for various two-dimensional lattices in quasi-2D silicon crystals suggested in the previous works, such as the two pair electromagnetically induced atomic gratings finished by Yanpeng Zhang, *et al.*(2011), the two dimensional atomic lattices prepared by Yiqi Zhang, *et al.*(2015), and the optically induced atomic lattices in atomic media completed by Zhaoyang Zhang, *et al.*(2016) [28-30]. Recently, two new two-dimensional silicon allotropes (Si-Cmma and Si-Pmma) with excellent energetic stability and positive dynamical stability have been proposed and investigated by first-principles calculations in the work of Na Zhou, et al. (2019) [31].

It may be considered as another route to prepare new 2D structures of silicon crystal by using some novel method. In the article, we have fabricated the quasi-2D structures of silicon crystal involving two kinds of silicene with the hexagonal lattice and the new rectangular lattice by using irradiation of coherent electron beam on the amorphous Si film produced by using pulsed laser deposition (PLD) method, where quasi-2D crystallizing occurs due to suitable transferring energy

of high speed electron in layer, originating from the Heisenberg principle related to $\Delta p \sim h/\Delta x$. We have investigated the dynamic stability of the new quasi-2D silicon structures using first-principle calculations, which has a real direct bandgap of 0.78eV near X region. We made a comparison between optimum quasi-2D structures of silicon crystal and ideal model of 2D structures of silicon crystal involving two kinds of the silicene with the hexagonal lattice and the new rectangular lattice in the simulating calculation. Total energy calculations using density functional theory (DFT) show that the energy band in the new quasi-2D silicon structures possesses a Dirac-cone shape. Our experimental and theoretical study expanded the new quasi-2D silicon structures and demonstrated the potential for new materials with desirable properties.

Here, we report a new method that is capable to synthesis silicene directly. It has been discovered in our experiment that the silicene crystal rapidly grows with irradiation of coherent electron beam on amorphous silicon film prepared by using PLD method on substrate. It is very interesting that the electronic irradiation promotes the growth of nanocrystal in silicene structure, whose physical mechanism may be originated from the nanoscale characteristics of electronic de Broglie wave which produces resonance to transfer energy for crystal atoms, where the electronic speed is very high due to the Heisenberg principle related to $\Delta mv \sim h/\Delta x$ in nanolayer. We all know in natural sciences, many analogous structures and properties occur on different size hierarchy, for example, in the sub-micrometer scale related to photonic de Broglie wavelength, the nanosecond or femtosecond laser was used to fabricate amorphous silicon film in hundreds nanometers scale completed by X.Shi *et al.* (2014) [32]; and in the nanoscale space related to electronic de Broglie wavelength, the coherent electron irradiation can be used to prepare silicon crystal structures in angstrom scale realized by W.Q.Huang, *et al.* (2012) [33].

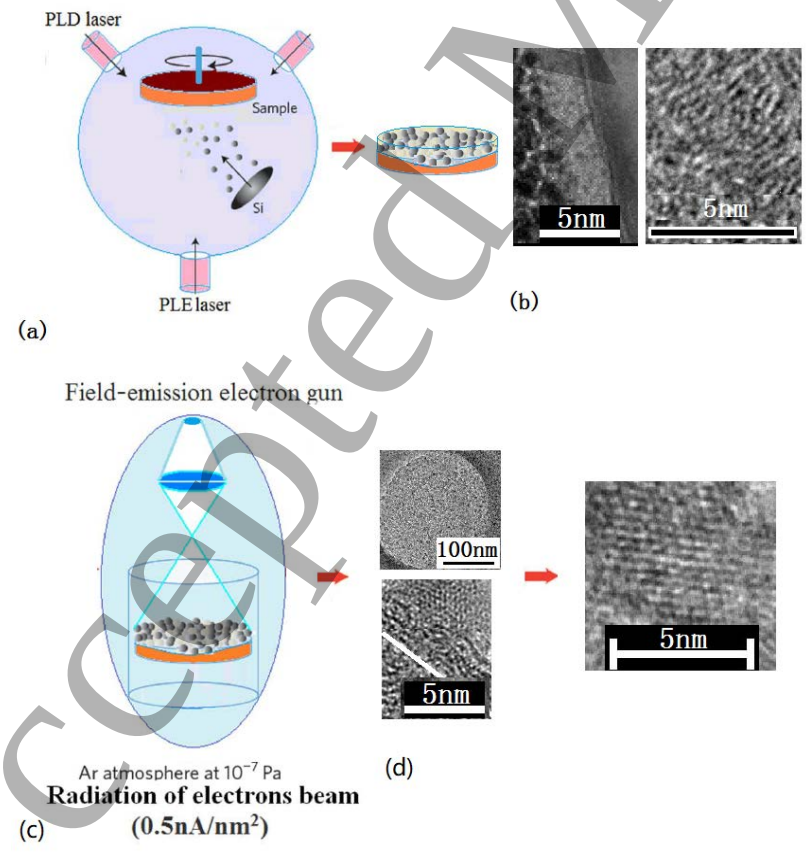


Fig.1 Preparation process of silicene crystal on amorphous carbon substrate
(a) Fabrication process of the amorphous silicon nanofilm by using PLD method
(b) TEM images exhibiting the nanofilm structure of amorphous silicon
(c) Preparing process of silicene crystal through interaction of coherent electron beam on the amorphous silicon nanofilm
(d) Left TEM image of spot shape occurred under the irradiation of coherent electron beam on surface, and the right TEM image of the silicene crystal

A silicon wafer (100) oriented substrate was taken on the sample stage in the PLD fabrication system. A pulsed Nd:YAG laser (wavelength: 1064 nm, pulse length: 60 ns, repetition rate: 1000) was used in PLD process. Figure 1 shows the synthesis process of the silicene, which involves novel two steps fabricating process: at first producing the amorphous silicon film by using PLD method, and then generating silicene crystallizing by using irradiation of coherent electron beam on the film. In the second process, the density of electron beam was about 0.5 nA/nm^2 from field-emission electron gun in the Tecnai G2 F20 system, accelerated by 200 KV, with higher energy and better coherent. In the irradiation under coherent electron beam, the silicene crystal was produced by controlling irradiating time from 20 to 30 min.

The PLD process is shown in Fig. 1(a), a nanosecond pulsed laser was introduced to silicon surface to form plasma of silicon ions and electrons, its interaction with silicon leads to the deposition of amorphous silicon film in nanoscale on the silicon surface. Figure 1(b) shows the cross sectional and top-view TEM images of the amorphous silicon layer, which was prepared on an amorphous carbon substrate. As shown in Fig.1(c), the detail growth process of the silicene crystal occurs under the irradiation of coherent electron beam with detail parameters on the amorphous silicon film. In Fig.1(d), the left picture exhibits TEM images of spot shape under irradiation of coherent electron beam on surface of the amorphous silicon film, and the right picture shows TEM image of the silicene crystal growing with interaction of coherent electron beam on surface.

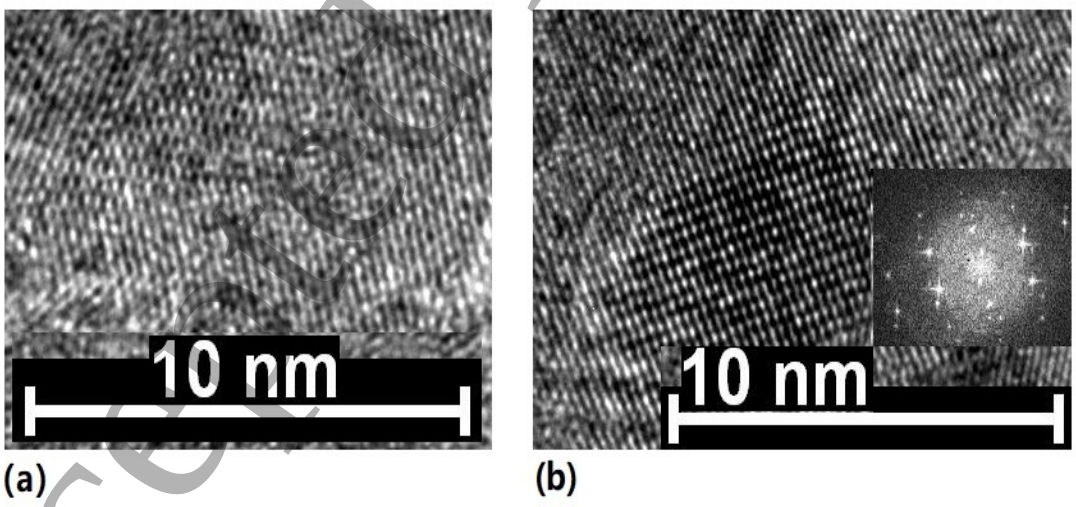


Fig.2 Silicene crystal observed in experiment
(a)TEM image of the silicene with the hexagonal lattice;
(b)TEM image of the new silicene with the rectangular lattice, in which the inset exhibits the electronic diffraction pattern of the rectangular lattice

It is important in the experimental result that besides the silicene with the hexagonal lattice was

observed in the TEM image of Fig.2(a), the new silicene crystal with rectangular lattice has been discovered under irradiation of coherent beam for 20~30min on the amorphous silicon nanofilm produced by using PLD method, as shown in the TEM image of Fig.2(b), in which the inset exhibits the electronic diffraction pattern on the 2D rectangular lattice. Here, the analysis of TEM image exhibits that the new silicene structure with rectangular lattice occurs in monoatomic layer on amorphous silicon. Here, the lattice constant is about 0.23nm, and the electronic diffraction pattern is related to the rectangular lattice.

The dynamic stability of the silicene was investigated by using first-principles calculations with consideration of two kinds of crystal structures observed in experiment, the hexagonal lattice and the new rectangular lattice. Their electronic behavior was investigated by an ab initio nonrelativistic quantum mechanical analysis. The density functional theory (DFT) was used to calculate the density of states (DOS) on Si 2D structures, which is carried out with the local density approximation (LDA) and gradient-corrected exchange-correlation function (GGA) for the self-consistent total energy methods. It is interesting in the total energy calculations using DFT that the quasi-2D structures of silicon crystal with the convex bonds occur in the lowest energy of optimum structure through the optimizing process on the ideal primal model of 2D silicon crystals.

At first, the ideal primal model of 2D silicon crystals with a hexagonal lattice can be exhibited in Fig.3(a) for its cross sectional structure and in Fig.3(b) for its top view before optimizing process in the simulating calculation, where the surface of the ideal primal 2D structure needs to be passivated by hydrogen atoms (white balls) which is a simple and effective treatment on surface dangling bonds in simulation. It should be noted after optimizing process that the quasi-2D structure with convex bonds is formed in a hexagonal lattice as shown in Fig,3(c), in which the convex bond angle of silicon atom on the quasi-2D is about 115°. Here, it is interesting to make a comparison between the silicene structure produced in optimized process of calculation as shown in Fig.3(c) and the silicene with the hexagonal lattice in the TEM image observed in the experiment as exhibited in and Fig.3(d), where they are very likely each other in the lattice shape.

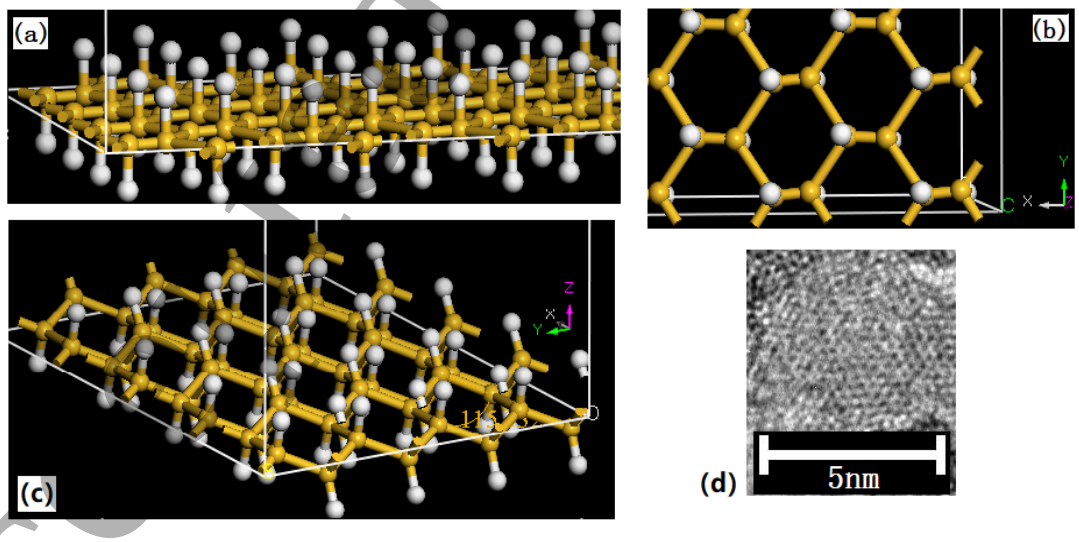
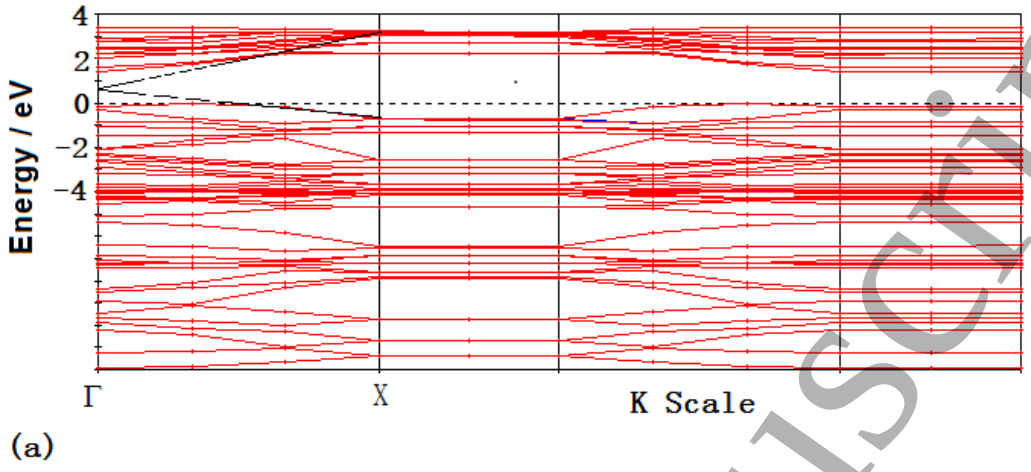
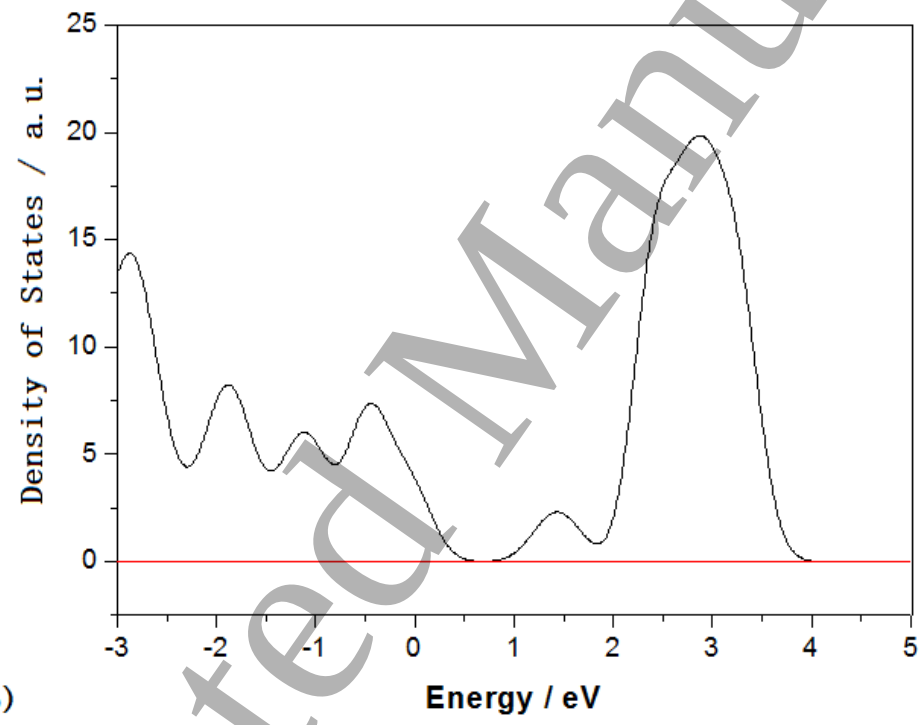


Fig.3 Simulation model of the ideal primal 2D-silicon with the hexagonal lattice passivated by hydrogen atoms (white balls). (a)Lateral crosscut structure of ideal primal model in the 2D structure with the hexagonal lattice; (b)Overlook structure of ideal primal model in the

2D structure with the hexagonal lattice; (c)Silicene structure with the hexagonal lattice after optimizing process in the simulating calculation, in which the convex bond angle of silicon atom is about 115°; (d)TEM image of silicene crystal with the hexagonal lattice observed in the experiment



(a)



(b)

Fig.4

(a) Energy band structure calculated in simulation model of the silicene with the hexagonal lattice, where it has a direct bandgap with gap of 1.4eV and a near Dirac-cone shape at Γ point

(b) Density distribution of states with localized peak near conduction band valley calculated in simulation model of the silicene with the hexagonal lattice

According to the simulation model of the silicene crystal with the hexagonal lattice related to the experimental result, the energy band was calculated to have a direct bandgap with gap of 1.4eV as shown in Fig.4(a), where a near Dirac-cone shape occurs at Γ point. The density of electronic states was calculated, as shown in Fig.4(b), in which the localized states occur in bandgap.

And then, let us investigate the new silicene structure with the rectangular lattice observed in

experiment by using first-principles calculations.

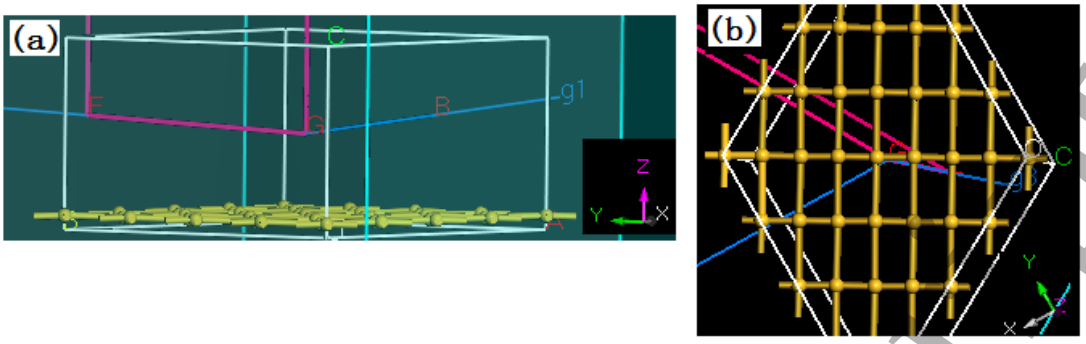


Fig.5 Simulation model of the 2D crystal with the rectangular lattice
(a) Lateral crosscut structure of ideal primal model of the 2D structure of silicon crystal with the rectangular lattice
(b) Overlook structure of ideal primal model of the 2D structure of silicon crystal with the rectangular lattice

The ideal primal model of 2D silicon crystals with the rectangular lattice in simulation was built as shown in Fig.5. The lateral crosscut and the overlook of ideal primal 2D rectangular lattice are exhibited in Fig.5(a) and (b). The rectangular lattice of the 2D structure of silicon crystal has a four-fold symmetry. The lattice points of a 2D Bravais lattice assumed to be in the xy plane, are given by the vectors: $X(l) = l_1\mathbf{a_1} + l_2\mathbf{a_2}$, where $\mathbf{a_1}$ and $\mathbf{a_2}$ are the primitive translation vectors of the lattice. And the diffraction points are described by $G(h) = h_1\mathbf{b_1} + h_2\mathbf{b_2}$, where $\mathbf{b_1}$ and $\mathbf{b_2}$, which are the primitive translation vectors of the reciprocal lattice. In the 2D Bravais lattices, the structure parameters for the rectangular lattice of the new 2D structure of silicon crystal are: $\mathbf{a_1}(a_0, 0)$, $\mathbf{a_2}(0, a_0)$, $\mathbf{b_1}$ $(2\pi/ a_0 (1, 0))$, $\mathbf{b_2}(2\pi/ a_0 (0, 1))$ and $a_c(a_0^2)$.

The interaction energy for the rectangular lattice of 2D silicon crystals in simulation can be optimized to keep lower for becoming more stable. In the geometry optimization, Figure 6(a) shows the change process of structure energy which is lower than that with the hexagonal lattice in the simulating calculation, where the structure parameters can be obtained through the optimization process in the DMol3 and the CASTEP modes. And figure 6(b) shows the new silicene structure with the rectangular lattice after optimizing process in the simulating calculation result, in which the convex bond angle of silicon atom is about 118°， the lattice constant is about 0.23nm and the thickness of atomic layer is about 0.12nm. The structure near monoatomic layer belongs to the fractional dimension of 2.1~2.5 in quasi-2D situation, and transforms to idea quantum-film shape, where new quantum phenomena and effects will appear in the process from the quasi-2D shape to the idea quantum-film.

The new silicene crystal with the rectangular lattice has been synthesized with interaction of electron beam on surface of amorphous silicon nanofilm produced by PLD method. Here, it is interesting to make a comparison between the new silicene structure in optimized calculation and the new silicene with the rectangular lattice in the TEM image observed in the experiment as exhibited in Fig.6(c). The new silicene crystal with the rectangular lattice is more stable, which was demonstrated in experimental observation for several months and in simulating calculation for the lowest binding energy of the structure.

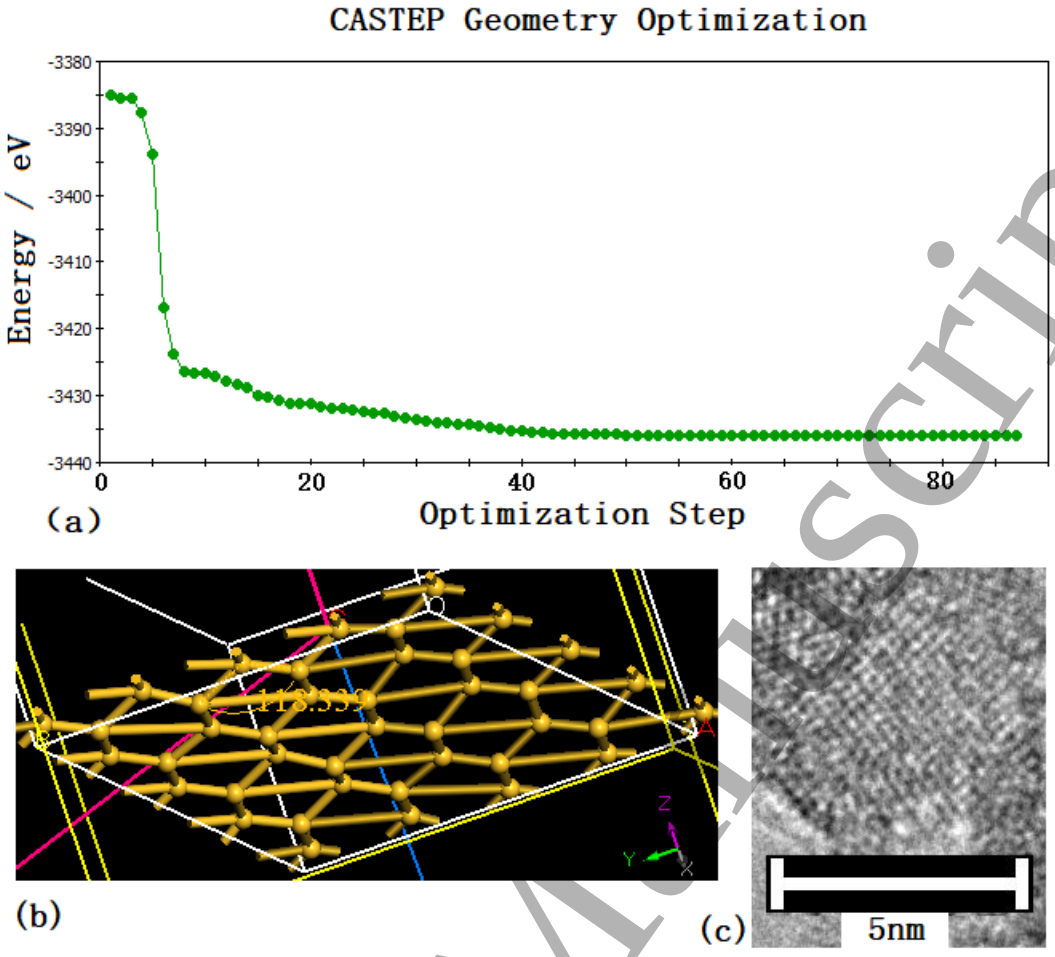


Fig.6 Change process in the CASTEP geometry optimization of the new silicene crystal with the rectangular lattice.

(a) Change process of structure energy in the optimization process

(b) New silicene crystal with the rectangular lattice after optimizing process in the simulating calculation, in which the convex bond angle of silicon atom is about 118°

(c) TEM image of the new silicene crystal with the rectangular lattice observed in the experiment

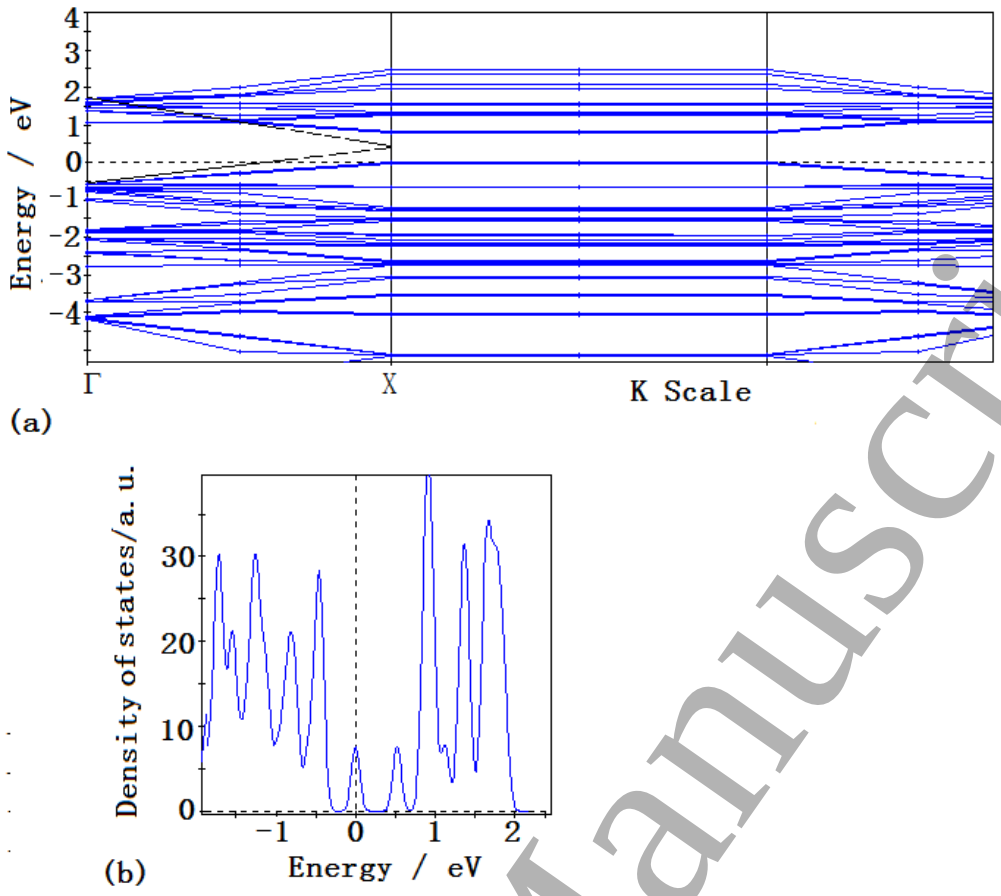


Fig.7

(a) Energy band structure obtained in calculation, where it has a real direct bandgap with gap of 0.78eV and a near Dirac-cone shape at X region in the new silicene crystal with the rectangular lattice

(b) Density distribution of states with localized peaks in bandgap calculated in simulation of the new silicene crystal with the rectangular lattice

According to simulation model of the new silicene crystal with the rectangular lattice related to the experimental result, the energy band structure was calculated to be exhibited in Fig.7(a), which has a real direct bandgap of 0.78 eV, where a near Dirac-cone shape occurs near X region. Here, the different bandgap from that in the silicene crystal with the hexagonal lattice may be originated from different combining energy. The density of electronic states was calculated as shown in Fig.7(b), where the localized peaks near Fermi level and conduction band valley occur in bandgap. Here, the direct bandgap of 0.78 eV (refer to wavelength of about 1500nm) on the new silicene crystal should have a good application in optic-communication window.

In conclusion, we have presented the discovery of a new method to synthesis the silicene directly by using irradiation of coherent electron beam on amorphous silicon film prepared by pulsed laser deposition. The resulting silicene structure exhibits a new rectangular lattice observed in experiment, where the rectangular lattice structure keeps at the lowest binding energy demonstrated in simulating calculation. The energy band properties were simulated by using first-principles calculations. The simulating calculation shows a direct bandgap of 0.78eV (refer to wavelength of about 1500nm) in the new silicene crystal with the rectangular lattice, where it should have a good application in optic-communication window. The total energy calculations

using DFT reveal that the new silicene structure has a near Dirac-cone like the energy band of graphene. It is interesting to observe the structures change between the silicene crystal after optimizing and the ideal primal model of 2D structures of silicon crystal in the simulating calculation, in which the convex atomic layers were found in the quasi-2D structures optimized replacing the plat atomic layer in the ideal primal model. The discovery of new silicene structures prepared on silicon directly and their theoretically predicted unique properties shed a light to conventional silicon material and open a new route towards era of nanoelectronic silicon devices.

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Competing interests
The authors declare no competing financial interests and no-financial interests.

新的硅烯结构制备及其特殊的能带性质

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摘要

与石墨烯具有二维六边形点阵结构类似，硅烯可能的结构及其性质也吸引着科学家们的研究兴趣。然而，自然界中并不存在像石墨烯一样的硅二维结构，近似六边形点阵的硅烯只是一种准二维结构。这里，我们报道了一种新的带有四边形点阵的硅烯结构被发现，采用相干电子束作用在非晶硅薄膜上能够生长这种新的结构，其非晶硅薄膜是用纳秒脉冲激光沉积方法（PLD）制备的，很有趣的是相干电子束将适当的动能输运到非晶硅原子上会形成快速晶化在表面生成这种新的硅烯结构。我们用第一性原理和密度泛函（DFT）方法模拟计算研究了这种新的硅烯结构，研究结果显示，这种带四边形点阵的准二维硅烯结构在其膜上会翘起 118°的角，这种拟合优化过的结构具有较低的键合能量，其能带结构具有 0.78eV 的直接带隙（这在光通信第三通道会有很好的应用）。

关键词：硅烯，纳米薄膜，相干电子束，脉冲激光，狄拉克锥

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