Monolayer-to-bilayer transformation of silicenes and their structural analysis

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Silicene, a two-dimensional honeycomb network of silicon atoms like graphene, holds great potential as a key material in the next generation of electronics; however, its use in more demanding applications is prevented because of its instability under ambient conditions. Here we report three types of bilayer silicenes that form after treating calcium-intercalated monolayer silicene (CaSi₂) with a BF₄⁻ -based ionic liquid. The bilayer silicenes that are obtained are sandwiched between planar crystals of CaF₂ and/or CaSi₂, with one of the bilayer silicenes being a new allotrope of silicon, containing four-, five- and six-membered sp³ silicon rings. The number of unsaturated silicon bonds in the structure is reduced compared with monolayer silicene. Additionally, the bandgap opens to 1.08 eV and is indirect; this is in contrast to monolayer silicene which is a zero-gap semiconductor.
A frenzy of interest in graphene has spawned many theoretical and experimental studies1–4. After calculating the structures of two-dimensional (2D) crystals of silicon (silicene)5–7, researchers have speculated that silicon atoms might form graphene-like sheets and have attempted to produce such silicene structures8–12. Very recently, Tao et al.13 succeeded in fabricating the first silicene transistor, although the device’s performance was modest. Nonetheless, the development of much more facile and practical processing methods has remained a challenging issue. The most difficult problem is that silicene grows on specific substrates and is stable only under vacuum conditions13,14,15. Another issue is that the influence of the substrate cannot be removed; the strong hybridization between Si and the substrate may stabilize silicene grown on specific substrates8,14–16.

In a previous report on calcium-intercalated silicene (CaSi2), we observed a massless Dirac-cone band dispersion at the k-point in the Brillouin zone, which was located far from the Fermi level. We observed a massless Dirac-cone band dispersion at the k-point in the Brillouin zone, which was located far from the Fermi level. Nonetheless, the development of much more facile and practical processing methods has remained a challenging issue. The most difficult problem is that silicene grows on specific substrates and is stable only under vacuum conditions13,14,15. Another issue is that the influence of the substrate cannot be removed; the strong hybridization between Si and the substrate may stabilize silicene grown on specific substrates8,14–16.

In a previous report on calcium-intercalated silicene (CaSi2), we observed a massless Dirac-cone band dispersion at the k-point in the Brillouin zone, which was located far from the Fermi level because of the substantial charge transfer from the Ca atoms to the silicene layer16. This result is similar to the previously reported band structures of silicene deposited on specific substrates9 because CaSi2 is a type of Zintl silicide, in which the formal charge is rewritten as Ca2+ and Si− (ref. 18). Therefore, the intrinsic electronic structure of silicene has never been observed. In the calculated results, a van der Waals bonded silicene layer has been deposited on an intact multi-CaF2 layer19. If the Ca layer of CaSi2 had been exchanged with a CaF2 layer, the influence of the substrate would have been almost completely suppressed. To reduce the influence of external factors on the electronic structure of silicene (for example, from substrates or counter ions) and to increase the stability under ambient condition, we replaced monolayer silicene with bilayer silicene.

The existence of a bilayer silicene structure, whose density of unsaturated silicon bonds is reduced in comparison with monolayer silicene, has been predicted by molecular dynamics (MD) calculations20–27. If we could experimentally prepare a similar bilayer silicene, we could then investigate its intrinsic electronic structure. Because of the electron transfer from the calcium cation, the monolayer silicene in CaSi2 is a formally anionic layer27; when the calcium cation becomes electrically neutral, the silicene will not retain its honeycomb structure and will reconstruct to form a more stable structure. Under this supposition, we attempted to segregate the Ca and Si phases while maintaining the layer structures by diffusing fluoride (F) atoms, which are more electronegative than Si, into CaSi2; the goal was to form an ionic bond (or interaction) between Ca and F. In this study, BF3 anion-based ionic liquid was used for the origin of fluoride anion.

**Results**

Fluoride diffusion into CaSi2. When the CaSi2 crystal (Supplementary Fig. 1) was annealed in [BMIM][BF4] ionic liquid at 250–300 °C, it was changed to a CaF2Fx (0 ≤ x ≤ 2.3) compound through diffusion of F−, in which the local F− concentration gradually decreased from the crystal edge to the interior (Fig. 1a,b and Supplementary Fig. 2). As a result, three types of bilayer Si in a CaSi2 single crystal were obtained by diffusion of F−. Figure 1c, which displays a high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) image taken of the CaSi2Fx1.8 compound, shows the alternate stacking of planar crystal domains with layer thicknesses of 1–2 nm. The HAADF-STEM imaging provided an atomic-scale Z-contrast image (Z: atomic number) to distinguish the heavier constituent elements28–30. STEM-energy-dispersive X-ray spectroscopy (STEM-EDX) elemental mapping identified the bright-contrast crystal domains, which were identified as the CaF2 phase and the dark domains, which were identified as Si phases (Fig. 1f–j). We determined the crystal structures of the entire planar region in the images of the CaSi2Fx1.8 and CaSi2Fx2.0 compounds shown in Fig. 1c,d, respectively. These planar domains were identified as trilayer CaF2, trilayer Si, bilayer CaF2, and a novel bilayer silicene (denoted as w-BLSi in Fig. 1c,d) that has not been previously predicted by MD calculations20–27. Furthermore, two types of bilayer silicenes, one with inversion symmetry (i-BLSi) and one with mirror symmetry (m-BLSi), were recognized in the CaSi2Fx0.6–1.0 composition area (Fig. 1e and Supplementary Fig. 3). The formation of m-BLSi is in accordance with predictions from a previous MD study27. The i- and m-BLSi are adjacent to a pair of CaF2 and CaSi2 crystal layers. The abundance ratio of i-BLSi to m-BLSi was 124:3 in the observed HAADF-STEM images. Because the calculated energy of i-BLSi was 0.03 eV per atom lower than that of m-BLSi under vacuum, the abundance ratio is qualitatively reasonable. The average size of w-BLSi is ~30 nm, and that of m-BLSi is ~10 nm. The size of i-BLSi is greater than 51 nm, which is the maximum size that can be observed by STEM imaging.

**Structural determination of w-BLSi.** The atomic structure of the bilayer silicene was determined from HAADF-STEM images that were taken with different incident electron beam directions (Fig. 2a–c, Supplementary Fig. 4 and Supplementary Note 1). As shown in Fig. 2d, the bilayer silicene structure had a 2D translation symmetry and a wavy morphology (hereafter, we refer to the structure as w-BLSi). The w-BLSi structure consists of two silicene layers, with alternating chair and boat conformations, that are vertically connected via four- and six-membered rings. Because w-BLSi consists of only Si atoms exhibiting tetrahedral coordination, the top atom of the five-membered silicon ring possesses unsaturated silicon bonds (dangling bonds). Therefore, compared with those in monolayer silicene and i- or m-BLSi, the density of unsaturated silicon bonds in w-BLSi decreased to 25 and 50%, respectively (Supplementary Fig. 5).

We determined the atomic positions of w-BLSi from high-resolution transmission electron microscopy and HAADF-STEM images as accurately as possible (Supplementary Figs 6 and 7, Supplementary Table 1 and Supplementary Note 2). The 2D translation periods of w-BLSi were a = 0.661(2) nm and b = 0.382(3) nm, and the two translation axes were normal to each other (Supplementary Fig. 8). The a period of w-BLSi is similar to the triple lattice spacing of d110 in CaF2 (0.223 nm), and the b period is similar to d110 in CaF2 (0.386 nm); that is, the difference between w-BLSi and CaF2 (111) is less than the observation error (Supplementary Fig. 9).

Because the atomic arrangement of the (111) plane of the CaF2 crystal exhibited threefold symmetry, three equivalent relative rotation angles were observed between w-BLSi and the CaF2 (111) plane (Supplementary Figs 10 and 11). In addition, the angle between the [010]w-BLSi and [111]w-BLSi directions was almost 60° (Supplementary Fig. 10, w-BLSi is described in 2D notation, because 2D can be expressed more simply than three dimensions). Therefore, Figs 1c and 2a show the contrast of two different arrangements of bright dots—specifically, the [010] and [11] direction images (Fig. 2c) in the w-BLSi regions. In almost all of the observed HAADF-STEM images, w-BLSi always faced the (111) plane of CaF2, and the F vacancies (red arrows in Fig. 1d) on the CaF2 (111) surface were recognized at special positions associated with the wavy structure of w-BLSi. A w-BLSi was observed to be sandwiched between two CaF2 layers with an F-site surface vacancy of ~0.5 at the interface (Fig. 1d, Supplementary Figs 7,12–15 and Supplementary Note 3).
DFT and \textit{ab initio} MD calculations and optical properties. The w-BLSi structure appears to resemble re-BLSi\textsuperscript{20} in appearance; however, its atomic arrangement is clearly different (Supplementary Fig. 16). An \textit{ab initio} MD calculation was performed for BLSi under the conditions corresponding to the experimentally observed structure, that is, BLSi was sandwiched between two CaF\textsubscript{2} layers with an F-site surface vacancy of 0.5 at the interface. The MD calculation was started with the i-BLSi structure, but it was immediately transformed to another BLSi structure. The system was then equilibrated, and the resultant BLSi structure was found to perfectly agree with the experimentally observed w-BLSi structure in Fig. 3a (Supplementary Tables 2–5, Supplementary Fig. 17 and Supplementary Note 4). The electronic density of states (DOS) for w-BLSi was calculated by using the structure in Fig. 3a, and the decomposed DOSs for Si, Ca, and F are shown in Fig. 3b. The Ca and F bands are located far below the Fermi level, and the valence bands consist of only Si bands. An ionic rather than a covalent interaction is thus expected between Si and Ca or F. We also observe that the bandgap opens to \(0.65\)\textit{eV}, in contrast to monolayer silicene, which is a zero-gap semiconductor\textsuperscript{31}. Interestingly, however, the gap closes when w-BLSi is isolated without geometry optimization under vacuum (Supplementary Fig. 18b). This result indicates that, in the CaSi\textsubscript{2}F\textsubscript{X} compound, charge transfer from Ca to Si occurs, filling the energy levels that are unoccupied under vacuum (Supplementary Discussion). Thus, the electronic properties of w-BLSi appear to be sensitive to its environmental conditions.

The presence of the F vacancies allows the electrons on Ca to transfer to Si, which enhances the stability of the w-BLSi structure (Fig. 3a) by saturating the dangling bonds. The CaF\textsubscript{2-X} domains (specifically, ionic crystalline domains) surrounding the Si layers are key to the formation of the w-BLSi structure.

The optical bandgap can be calculated from the absorption spectrum. The diffuse reflectance spectrum of the powder sample with CaSi\textsubscript{2}F\textsubscript{1.8-2.3} composition was measured, and the obtained reflectance spectrum data (Supplementary Fig. 19) were converted to a Kubelka–Munk function (K/S), which is proportional to the absorption coefficient (\(\alpha\)). The sample was a mixture of w-BLSi, two types of trilayer silicene (with dangling bonds and terminated with F atoms, as shown in Supplementary Fig. 20) and a CaF\textsubscript{2} layer (Supplementary Note 5). The relationship between the absorption coefficient (\(\alpha\)) and the bandgap energy (\(E_g\)) can be described by two types of equations: \(\alpha h v = \text{const} (\text{direct gap})\) and \(\alpha h v = A (h v - E_g)\) (indirect gap), where the DOS for 2D crystals is constant as a function of energy\textsuperscript{32–35} (Supplementary Note 5). Here, \(h\), \(v\) and \(A\) are Planck’s constant, light frequency and proportional constant, respectively. From two linear fittings of the spectrum, the latter equation was found to be suitable for the sample. The absorption edges of the CaSi\textsubscript{2}F\textsubscript{1.8-2.3} compound were observed at \(1.08\) and \(1.78\)\textit{eV} (Fig. 3c), assuming indirect transitions.

Freestanding trilayer silicene is semi-metallic, as shown by density functional theory (DFT) calculations\textsuperscript{36}. It has been suggested that the bandgap of trilayer silicene with dangling bonds in CaSi\textsubscript{2}F\textsubscript{1.8-2.3} is nearly zero if charge transfer between the...
trilayer silicene and the CaF2 layer is inhibited. From previous DFT results of monolayer and multilayer silicene terminated with atoms, it is conjectured that the bandgap of F-terminated trilayer silicene would be $1 \text{ eV}$ within the framework of the DFT and Perdew, Burke and Ernzerhof (PBE) technique. It should be noted that DFT calculations using a standard generalized gradient approximation functional tend to underestimate the bandgap (roughly $2/3$ in crystal Si). This indicates that the bandgap experimentally measured for the trilayer silicene should be $1.5 \text{ eV}$. Meanwhile, the bandgap for w-BLSi, which is estimated to be $0.65 \text{ eV}$ in the DFT–PBE calculation, is expected to be $\sim 1 \text{ eV}$ in the experimental measurement. Therefore, the measured gaps were estimated such that the gaps of w-BLSi and F-terminated trilayer silicene were 1.08 and 1.78 eV, respectively.

**Transformation process from monolayer silicene to w-BLSi.** On the basis of the HAADF-STEM data, we discussed a model for the transformation process from a monolayer silicene in CaSi2 (Fig. 4a) to w-BLSi (Fig. 4f). When F$^-$ ions diffuse from the surface of a CaSi2 crystallite into the crystal along the Ca layer,
thin CaF$_2$$_x$ planar crystals are formed; as a result, anionic silicene layers assemble to reduce the number of unsaturated bonds beyond the Ca layer (Fig. 4b). During this movement, the Si covalent bonding network with honeycomb symmetry is broken and its arrangement consequently becomes random (Fig. 4c). As shown in Fig. 4d, two types of bilayer silicenes, i-BLSi and m-BLSi, which formed in the slit-like regions, as predicted by the MD calculation$^{22}$, co-exist with CaSi$_2$ in the low F-concentration region. Both of these structures are stabilized as a result of charge transferred from the Ca atoms which saturate the silicon dangling bonds. With increasing F content, i- (or m-) BLSi is transformed to w-BLSi. Additionally, the structure possesses an indirect bandgap of 1.08 eV in contrast to monolayer silicene, which is a zero-gap semiconductor.

**Methods**

**Synthesis of CaSi$_2$Fx compound.** CaSi$_2$ single-crystal grains (0.1 g) were reacted with 5 ml of ionic liquid [BMIM][BF$_4$] (1-butyl-3-methylimidazolium tetrafluoroborate) at 300 $^\circ$C for 15 h. BF$_4$$^-$ decomposed into F$^-$ during annealing, and the CaSi$_2$ crystal was changed to CaSi$_2$Fx compounds ($0 \leq x \leq 2.2$) through the diffusion of F$^-$ (Fig. 1a,b). More details are given in Supplementary Method.

**Chemical composition analysis.** The chemical compositions of the CaSi$_2$Fx domains were determined by electron probe microanalyser (EPMA) with a wave dispersion system (JEOL JXA-8200), an accelerating voltage of 10 kV, and an electron irradiation area of 3 $\mu$m. Single-phase CaF$_2$ and Si crystals were used as the standard for quantitative composition analysis of Ca, F and Si. EPMA line analyses were performed with 5 $\mu$m steps from the edge to the inside of the CaSi$_2$Fx crystallites cross-sectioned parallel to the CaSi$_2$ [001] direction.

**TEM/STEM analysis.** HAADF-STEM observations$^{28–30}$ and STEM energy-dispersive X-ray spectroscopy (EDX) analyses were performed with a Titan, G2 60–300 electron microscope (FEI, Cs = 156 nm) operated at 300 kV. HAADF-STEM imaging was capable of providing an atomic-scale Z-contrast image associated with the heavier constituent elements. The annular detector was set to collect the electrons scattered at angles between 50.5 and 200 mrad. High-resolution transmission electron microscopy observations were obtained with a JEM-2000EX electron microscope (JEOL, Cs = 0.7 mm) operating at 200 kV. TEM specimens of CaSi$_2$Fx were detected with five different F concentration ranges (CaSi$_2$F$_{0.6-1.0}$, CaSi$_2$F$_{1.6}$, CaSi$_2$F$_{1.8}$, CaSi$_2$F$_{2.0}$, CaSi$_2$F$_{2.3}$) through the F$^-$ diffusion.

**Discussion**

We focused on calcium-intercalated silicene (CaSi$_2$) and discovered a strategy for transforming monolayer silicene into a novel bilayer silicene (w-BLSi). From HAADF-STEM images, we observed that w-BLSi was formed between the planar crystals of CaF$_2$ and contained four-, five- and six-membered silicon rings, although w-BLSi consists of only Si atoms exhibiting tetrahedral coordination. Compared with monolayer silicene, the number of unsaturated silicon bonds in w-BLSi decreased to 25% of the unit cell. The transformation process from monolayer silicene in CaSi$_2$ to w-BLSi was estimated from HAADF-STEM data. When F$^-$ ions diffuse into the CaSi$_2$ crystal along the Ca layer, thin CaF$_2$$_x$ planar crystals and two types of bilayer silicenes (i-BLSi and m-BLSi) are formed, following breakage of the Si covalent bonding monolayer network. Both of these Si structures were stabilized as a result of charge transferred from the Ca atoms with CaF$_2$$_x$. F diffusion in CaSi$_2$. (a) A random arrangement of i-BLSi and bilayer CaF$_2$$_x$ in CaSi$_2$. (b) i-BLSi, CaF$_2$$_x$ and CaSi$_2$ in a region with CaSi$_2$F$_{0.6-1.0}$. (c) i-BLSi and w-BLSi formed within the same layers in CaSi$_2$F$_{0.6-1.0}$. (f) w-BLSi in CaSi$_2$F$_{2.0}$. All scale bars, 1 nm.

Figure 4 | A model for the transformation process from monolayer Si to w-BLSi. (a) and (d–f) HAADF-STEM image. (b,c) A schematic model. (a) Raw tr6 CaSi$_2$. (b) F diffusion into CaSi$_2$. (c) A random arrangement of i-BLSi and bilayer CaF$_2$$_x$ in CaSi$_2$. (d) i-BLSi, CaF$_2$$_x$ and CaSi$_2$ in a region with CaSi$_2$F$_{0.6-1.0}$. (e) i-BLSi and w-BLSi formed within the same layers in CaSi$_2$F$_{0.6-1.0}$. (f) w-BLSi in CaSi$_2$F$_{2.0}$. All scale bars, 1 nm.
Optical reflectivity. Diffuse reflectance spectra were obtained for the CaSi2 films, which were prepared by co-evaporation of Ca and Si. The diffuse reflectance spectra were processed under the Kubelka–Munk formalism, and the bandgaps were determined using a plot of the multiplication of the K/S and energy. More details are given in Supplementary Methods.

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Author contributions

R.Y. and H.N. conceived the idea. R.Y. and T.O. designed the experiments. R.Y. and H.N. synthesized the CaSi2 single crystals and CaSi2FX compounds. Y.H. performed the HAADF-STEM observations and the EDX analyses. T.M. and M.J.S.S. performed the theoretical work. R.Y. and T.O. characterized the w-BLS. R.Y., T.O., T.M. and H.N. wrote the manuscript. All the authors have read the manuscript and agree with its content.

Additional information

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