3 Two-dimensional silicon nanosheets

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3.1 INTRODUCTION
Since the discovery of graphene, a single-atom-thick honeycomb carbon structure, a great deal of effort has been both theoretically and experimentally dedicated to the search for similar two-dimensional (2D) materials comprising group-IV elements, especially silicon. The silicon equivalent of graphene was first theoretically proposed and later reinvestigated, which renamed it silicene (Takeda and Shiraishi 1994; Guzman-Verri and Voon 2007). In those reports, silicene was described as a single-atom-thick silicon crystalline material with a honeycomb lattice comprising $sp^2$ silicon bonds. Therefore, silicene is not a naturally occurring material and a solid phase of silicon similar to graphite is lacking in nature. Thus, pure silicene layers cannot be obtained by exfoliation methods as initially performed in the case of graphene, and more sophisticated methods have to be considered for the growth or synthesis of silicene.

Silicene was first synthesized by following a bottom-up approach in which silicon was deposited on metal surfaces that do not strongly interact with Si atoms or the resultant compounds. Ag surfaces have been recently used to grow Si superstructures and to grow massively parallel Si nanoribbons on Ag(001) and Ag(110) surfaces, respectively (Sahaf et al. 2007; De Padova et al. 2008; De Padova et al. 2010). These nanoribbons were shown to comprise hexagonal honeycomb-like Si-based unit cells, in agreement with density functional theory (DFT) calculations (Kara et al. 2009; De Padova et al. 2011).
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These structures were also shown to have a linear electronic dispersion similar to massless relativistic Dirac fermions, which can be seen as the first evidence of a local silicene-like arrangement with \( sp^2 \)-hybridized Si atoms. Subsequently, in 2012, actual 2D silicene sheets were formed on Ag(111) surfaces with a sixfold top-layer symmetry (Vogt et al. 2012). In 2015, the first silicene transistor was synthesized by a tricky process with modest performance and lifetime (i.e., measured in minutes) characteristics (Tao et al. 2015). This work was surprising to many researchers, and the silicene transistor field is rapidly progressing.

Although graphene is the most conductive substance known, it lacks a crucial characteristic. Unlike the semiconductors used in computer chips, graphene lacks the band gaps required to switch on and off and to perform “logical” operations on bits. On the other hand, silicene has a band gap since some of its atoms buckle upwards to form corrugated ridges, thereby slightly modifying the energy state of some electrons. However, handling silicene in the laboratory has been extremely challenging. Thus, silicene deposited under high-vacuum conditions almost comprises \( sp^2 \) silicon, which is easily oxidized under ambient conditions. Therefore, if silicene is to be used under ambient conditions, 2D silicon nanosheets (SiNSs) with \( sp^3 \) silicon bonds should be selected. The SiNSs described here are defined as compounds having silicon bonding with \( sp^3 \) hybridization.

In contrast to conventional physical methods (i.e., deposition of silicene), soft chemical synthesis is one candidate for methods and they are anticipated to receive significant attention for a wide range of applications. The chemical reaction of organosilicon compounds is a simple, gentle method to build up silicon nanomaterials. For example, silicon nanoparticles can be synthesized by reacting tetrachlorosilane with the Zintl compound (Teo and Sun 2007). However, the synthesis of 2D nanocrystalline silicon structures is complex compared with cluster structures. Thus, the reaction of trihalosilane with alkali metals was expected to synthesize 2D SiNS, but amorphous bridged polysilane compounds and/or small silicon clusters were obtained instead.

According to previous reports on metal-oxide nanosheets (Wang and Sasaki 2014), exfoliation is a reliable approach for synthesizing SiNS from isotropic 2D silicon compounds. The complete list of layered silicon compounds includes Zintl CaSi2, layered polysilane (\( Si_6H_6 \)), and siloxene (\( Si_6H_3(OH)_3 \)), which are crystalline layered structures composed of buckled 2D silicon sublattices similar to the (111) plane of diamond-type Si. Single silicon layers of \( Si_6H_6 \) and \( Si_6H_3(OH)_3 \) were stabilized through termination with hydrogen or hydroxyl groups placed out of the layer plane. These layered silicon compounds are composed of \( sp^3 \) silicon bonding. Although the single layers in these materials weakly interact with each other, they are not easily exfoliated, therefore, the solubility into organic or inorganic solvents is very low. Thus, some modifications of the silicon surface are required to obtain 2D SiNS. Here we summarize the main characteristics of 2D silicon compounds, along with the synthetic methods of SiNS and some properties of these materials.

### 3.2 MONOLAYER SILICENE COMPOUNDS

#### 3.2.1 GROWTH OF CALCIUM-INTERCALATED SILICENE, CaSi2

CaSi2, one of the Zintl phases (Zintl 1939; Schäfer et al. 1973), is an intermetallic compound formed between a strongly electropositive metal (e.g., alkali metals and alkaline earth metals) and a somewhat less electropositive atom such as Si. CaSi2 has a 2D silicon subnetwork resembling buckled Si(111) planes in which the Si6 rings are interconnected with \( sp^3 \) bonds while the puckered (Si6)3 polyanion layers are separated by planar monolayers of Ca2+. CaSi2 has a trigonal structure (space group R-3m) at ambient pressure, which can only vary in its stacking sequence to give rise to tr6 (\( a = 0.3855 \) nm, \( c = 3.062 \) nm) (Evers 1979) and tr3 (\( a = 0.3829 \) nm, \( c = 1.590 \) nm) (Dick and Ohlinger 1998) polymorphs. In tr6 CaSi2, the stacking of the trigonal Ca layers follows an AABCC sequence with a six-layer repeat distance (Figure 3.1a and b). Tr3 CaSi2 has a three-layer repeat distance, with the Ca layers stacked following an ABC sequence (Figure 3.1c). CaSi2 ingots typically crystallize in the tr6 polymorph. Thus, it has been reported that only 3 out of more than 200 samples crystallized in the tr3 polymorph (Dick and Ohlinger 1998). Tr3 CaSi2 is more stable than its tr6 counterpart. Additionally, the calculated Gibbs energy relation suggests that tr6 CaSi2 stabilizes over tr3 with higher temperature (Nedumkandathil et al. 2015). It has been speculated that impurities and/or defects stabilize the tr3 CaSi2 phase (Evers 1979; Vogg et al. 1999; Nedumkandathil et al. 2015).
Several CaSi₂ single-crystal growth experiments have been reported. Single-crystal specimens with lateral sizes of 8 × 8 mm and 5 × 5 mm were obtained by slow cooling of ingots (Evers and Weiss 1974; Yamanaka et al. 1981). Using the floating zone method, a CaSi₂ single crystal with a diameter of 10 mm and length of 100 mm was also fabricated (Hirano 1991). The generally accepted Ca–Si binary phase diagram indicates that the process CaSi + liquid → CaSi₂ occurs as a metastable peritectic reaction in the high-purity melt, on the other hand, the stable peritectic reaction Ca_{14}Si_{19} + liquid → CaSi₂ takes place at CaSi₂ stoichiometric compositions when the melt contains some impurities (Figure 3.2a) (Yaokawa et al. 2014). A CaSi₂ single phase is formed from the high-purity stoichiometric CaSi₂ melt by using 5N Ca and 5N Si as starting materials while slightly undercooling (by only 5°C). Thus, a tr6 CaSi₂ single-phase ingot can be obtained by casting at 1–100°C/min cooling rates (Figure 3.2b through d).

### 3.2.2 ELECTRONIC PROPERTIES OF MONOLAYER SILICENE IN CaSi₂

CaSi₂, considered a calcium-intercalated silicene, provides a good opportunity to investigate the intrinsic electronic structure of genuine silicene. While the Si atoms in CaSi₂ form a hexagonal 2D layer, silicene synthesized on a silver substrate has been reported to have a different structure (i.e., dumbbell structure) (Cahangirov et al. 2014). In CaSi₂, the Ca atoms are considered to play a role in stabilizing the buckled honeycomb network structure of Si atoms by donating electrons to the silicene layers (Cahangirov et al. 2009; Rui et al. 2013).

The electronic properties (i.e., band structure) of silicene in a tr3 CaSi₂ single crystal can be analyzed by high-resolution angle-resolved photoemission spectroscopy (ARPES). From the X-ray diffraction (XRD) patterns of the powder and the single-crystal samples (Figure 3.3a and b), the grown tr3 CaSi₂ crystal reveals the high-quality crystal. Low-energy electron diffraction (LEED) measurements of the cleaved surface also show a clear 1 × 1 pattern, thereby indicating that no reconstruction of the crystal structure took

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Figure 3.1 (a) HAADF-STEM image of tr6 CaSi₂. (b) Model of tr6 CaSi₂. (c) Model of tr3 CaSi₂.

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Figure 3.3 (a) HAADF-STEM image of tr6 CaSi₂. (b) Model of tr6 CaSi₂. (c) Model of tr3 CaSi₂.
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Figure 3.2 (a) Phase diagram of the Ca–Si binary system around CaSi₂ obtained on the basis of differential thermal analysis (DTA) results. Top-surface pictures of ingots fabricated from Ca_{1.00}Si₂ melt at varying cooling rates: (b) 1, (c) 10, and (d) 100°C/min, respectively.

Figure 3.3 (a) XRD pattern from the tr3 CaSi₂ crystal powder sample. (b) XRD pattern from the (111) cleavage plane of a CaSi₂ single crystal. (c) LEED pattern from the (111) cleavage plane of a CaSi₂ crystal measured with a primary electron energy of 80 eV. (d) High-resolution ARPES spectra near the Dirac point at ca. the K(H) point in tr3 CaSi₂. (e) ARPES intensity plot around the K(H) point as a function of the wave vector and the binding energy. The peak position in the ARPES spectra, obtained by fitting with Lorentzians, is shown by blue and red circles. (f) Second-derivative ARPES intensity plot around E_D.
place at the surface (Figure 3.3c). In the ARPES-derived band structure, a massless Dirac cone of dispersed \( \pi \) electrons at the K(H) point in the Brillouin zone is clearly observed, together with \( \sigma \)-band dispersions at the \( \Gamma \) point (Noguchi et al. 2015). Furthermore, the Dirac point is located at ca. 2 eV from the Fermi level \( (E_F) \), thereby revealing a substantial charge transfer from the Ca atoms to the silicene layers (Figure 3.3d through f). The ARPES results indicate that the \( sp^2 \) bonding framework essentially holds the CaSi\(_2\) structure, thereby producing the massless Dirac-cone state at the \( K \) point despite the strongly buckled structure of the silicene layers (i.e., the graphene-like electronic structure is stably formed in this metal-intercalated multilayer silicene).

### 3.3 Bilayer Silicene Compounds

Although it is required for the preparation of practical and adaptable silicene transistors (Tao et al. 2015), the development of significantly more facile and practical processing methods has remained a challenging issue. The most relevant issue is that silicene grows on specific substrates and is stable only under vacuum conditions (Fleurence et al. 2012; Gao and Zhao 2012; Vogt et al. 2012; Morishita et al. 2013). Another issue lies in avoiding the influence of the substrate. Thus, the strong hybridization between Si and the substrate may stabilize silicene grown on specific substrates (Gao and Zhao 2012; Vogt et al. 2012; Cahangirov et al. 2013). Provided these limitations are overcome, silicene could be seriously considered as a next-generation high-efficiency platform for a wide variety of electronic applications. The experimental challenge with forming 2D silicon compounds is that the silicon tetrahedral bonding makes it difficult to exfoliate into silicene without using capping or functionalization with organic molecules (Okamoto et al. 2010; Sugiyama et al. 2010). However, the existence of an unfunctionalized 2D bilayer Si structure has been predicted by molecular dynamics (MD) calculations. Thus, several types of bilayer silicene were predicted to form in a slit-like pore or vacuum (Morishita et al. 2008; Bai et al. 2010; Johnston et al. 2011; Morishita et al. 2011; Cahangirov et al. 2014; Guo and Oshiyama 2014; Pflugradt et al. 2014; Sakai and Oshiyama 2015). One type of bilayer Si structure that is predicted to form under vacuum conditions (i.e., re-BLSi or reconstructed bilayer Si) has an unusual atomic arrangement consisting of two Si monolayers connected via four-, five-, and six-membered rings while retaining the tetrahedral coordination. However, such a bilayer Si structure has been predicted exclusively in computer simulations, and no one has succeeded in experimentally preparing this material to date.

#### 3.3.1 Synthetic Methods

Experimentally, three types of bilayer silicene can be synthesized from CaSi\(_2\). After annealing in an ionic liquid (i.e., [BMIM][BF\(_4\)]) at 250–300°C, a CaSi\(_2\) single crystal is transformed into a CaSi\(_2\)\(_{F_x}\) (0 \( \leq x \leq 2.3 \)) compound through the diffusion of F\(^-\). The concentration gradually decreases from the crystal edge to the interior (Figure 3.4a and b). STEM-EDX elemental mapping identifies the dark and bright crystal domains as CaF\(_2\) and Si phases, respectively (Figure 3.4c through g). These planar domains are identified as trilayer CaF\(_2\), trilayer Si, bilayer CaF\(_2\), and a novel bilayer silicene (denoted as w-BLSi in Figure 3.4g and h) in the CaSi\(_2\)\(_{F_{1.8}}\) and CaSi\(_2\)\(_{F_{2.0}}\) compounds shown in Figure 3.4b. Furthermore, two types of bilayer silicenes (i.e., inversion symmetry [i-BLSi] and mirror symmetry [m-BLSi] silicenes) are recognized in the CaSi\(_2\)\(_{F_{8.6-1.0}}\) composition area (Figure 3.4i). The formation of m-BLSi is in accordance with previous MD predictions (Morishita et al. 2008). The i- and m-BLSi structures must be adjacent to a pair of CaF\(_2\) and CaSi\(_2\) crystal layers. The abundance ratio of i-BLSi to m-BLSi is 124:3, as observed in the HAADF-STEM images. Since the calculated energy of i-BLSi is 0.03 eV/atom lower than that of m-BLSi under vacuum conditions, the calculated abundance ratio is qualitatively reasonable.

#### 3.3.2 Structural Determination of Bilayer Silicene

Bilayer silicene generally exists as a multiphase compound in CaSi\(_2\)\(_{F_x}\). Thus, the lattice constants and atomic positions of w-BLSi cannot be directly characterized by XRD. HAADF-STEM images at high magnification with atomic resolution often suffer distortion owing to specimen drift during scanning. Thus, the atomic structure of the bilayer silicene can be determined from HAADF-STEM images taken at...
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Figure 3.4 (a) Cross-sectional back-scatter detector (BSE) image of the crystal grain including a CaSi$_2$F$_x$ compound. (b) Electron probe micro-analysis (EPMA) quantitative line analysis result along the red arrow in (a). (c–f) STEM-EDX elemental mapping results of the CaSi$_2$F$_x$ composition region. One-element mapping (c: Si, d: Ca, and e: F). (f) Overlapped mapping of Si, Ca, and F. (g) HAADF-STEM image of the STEM-EDX elemental mapping area. (h) An enlarged HAADF-STEM image taken from a CaSi$_2$F$_x$ region in (b); red arrows indicate an F-vacancy site. (i) HAADF-STEM image taken from a CaSi$_2$F$_{0.6-1.0}$ region in (b); a bright spot contrast, corresponding to the projected atomic positions of m- and i-BLSi, can be observed in the image.

different incident electron beam directions (Figure 3.5a through c). As shown in Figure 3.5d, the w-BLSi structure has 2D translational symmetry and a wavy morphology. This structure consists of two silicenes in alternating chair and boat conformations, which are vertically connected via four-, five-, and six-membered rings. Figure 3.5e through h indicates the corresponding structural models projected in each direction. Since w-BLSi exclusively consists of Si atoms with tetrahedral coordination, the top atom of the five-membered silicon ring possess unsaturated silicon bonds (i.e., dangling bonds). Therefore, compared with monolayer silicene and i- (or m-) BLSi, the density of unsaturated silicon bonds in w-BLSi decreases by 25 and 50%, respectively.

The 2D translational periods of w-BLSi are calculated to be $a = 0.661(2)$ nm and $b = 0.382(3)$ nm, with the two translational axes being normal to each other. The $a$ period of w-BLSi is similar to the triple lattice spacing of $d_{112}$ in CaF$_2$ (0.223 nm), while the $b$ period is similar to that of $d_{110}$ in CaF$_2$ (0.386 nm). Thus, the difference between w-BLSi and CaF$_2$(111) is lower than the observation error. Since the atomic arrangement of the (111) plane in a CaF$_2$ crystal exhibited threefold symmetry, three equivalent relative rotation angles are observed between w-BLSi and the CaF$_2$(111) plane (Figure 3.6a). In addition, the angle between the [01]w-BLSi and the [11]w-BLSi directions is nearly 60° (Figure 3.6b). Nearly all the HAADF-STEM images reveals w-BLSi facing the (111) plane of CaF$_2$, with the F vacancies (red arrows in Figure 3.4b) on the CaF$_2$(111) surface being recognized at special positions associated with the wavy structure of w-BLSi.
3.3 Bilayer silicene compounds

Figure 3.5 (a–c) HAADF-STEM and simulation (insets) images of w-BLSi. (a) [01]w-BLSi and [11]w-BLSi incident directions ([1-10]CaF$_2$), (b) [10]w-BLSi, [11-2]Si, and CaF$_2$ directions. (c) [13]w-BLSi, [11-2]Si, and CaF$_2$ directions. (d) Schematic illustration of the w-BLSi atomic structure. (e–h) Schematic structures projected in each direction in e [01], f [13], g [11], and h [10] directions.

Figure 3.6 (a) Atomic positions in the interface between the w-BLSi (001) and the CaF$_2$ (111) plane. (b) Three equivalent relative rotation angles between w-BLSi and the CaF$_2$(111) plane.
3.3.3 BAND STRUCTURE

The w-BLSi structure apparently resembles that of re-BLSi (Morishita et al. 2011), although their atomic arrangements are clearly different. *Ab initio* MD calculations were performed for BLSi under the conditions corresponding to the experimentally observed structure (i.e., BLSi sandwiched between two CaF₂ layers with an F-site surface vacancy of 0.5 at the interface). If the MD calculations were started with i-BLSi, this structure would have been immediately transformed to another BLSi structure. The system is subsequently equilibrated, and the resultant BLSi structure is found to perfectly agree with the experimentally observed w-BLSi structure shown in Figure 3.7a. The electronic density of states (EDOSs) for w-BLSi was calculated by the structure in Figure 3.7a, and the decomposed DOS for Si, Ca, and F are shown in Figure 3.7b. The Ca and F bands are located far below the Fermi level, with the valence bands exclusively consisting of Si bands. Unlike a zero-gap semiconductor such as a monolayer (Huang et al. 2013), the band gap of these materials opens to ca. 0.65 eV. The presence of the F vacancies allows the electrons on Ca to be transferred to Si, thereby enhancing the stability of the w-BLSi structure by saturating the dangling bonds. The CaF₂−xF domains (i.e., ionic crystalline domains) surrounding the Si layers are key to the formation of the w-BLSi structure.

The optical band gap of w-BLSi can be measured from the absorption spectrum of the powder CaSi₂F₁.₈–₂.₃ sample, although this sample is a mixture of w-BLSi, two types of trilayer silicene, and a CaF₂ layer. The DOS for the 2D crystal is constant with energy \( D(E) = \text{const.} \) (in a three-dimensional (3D) crystal: \( D(E) \propto E^{3/2} \)). Therefore, the relationship between the absorption coefficient and the band gap energy can be described by the equations \( \alpha h\nu = \text{const.} \) (direct gap) and \( \alpha h\nu = A (h\nu - E_g) \) (indirect gap), where \( \alpha, h, \nu, A, \) and \( E_g \) are the absorption coefficient, Planck’s constant, the light frequency, the proportional constant, and the band gap, respectively (Lee et al. 1969; Gaiser et al. 2004; Mak et al. 2010; Bianco et al. 2013). In the case of the 3D crystal, this equation becomes \( \alpha h\nu^n = A (h\nu - E_g) \), where \( n = 1/2 \) and 2 indicate direct and indirect transitions, respectively. Thus, the absorption coefficient of an indirect gap is proportional to the energy, whereas that of a direct gap is constant. The diffuse reflectance spectrum is converted to the Kubelka–Munk function (K-M), which is proportional to the absorption coefficient, as shown in Figure 3.7c. Assuming indirect transitions, the absorption edges of the CaSi₂F₁.₈–₂.₃ compound are 1.08 and 1.78 eV. From previous DFT results on monolayer and multilayer silicenes terminated with atoms (Morishita et al. 2010; Gao et al. 2012), it is conjectured that the band gap of F-terminated trilayer silicenes should be ca. 1 eV within the framework of DFT and the Perdew, Burke, and Ernzerhof technique. It should be noted that DFT calculations using a standard generalized gradient approximation functional tend to underestimate the band gap (by ca. 2/3 in crystal Si). This indicates that the band gap experimentally measured for the trilayer silicene should be ca. 1.5 eV. The band gap for w-BLSi, which was estimated to be ca. 0.65 eV via DFT–PBE calculations, is expected to reach ca. 1 eV in experimental measurements. Therefore, the measured gaps are estimated to be 1.08 and 1.78 eV for w-BLSi and F-terminated trilayer silicenes, respectively.

![Figure 3.7](image-url)

**Figure 3.7** (a) Structure of w-BLSi sandwiched between two CaF₂ crystals, with vacancies at half of the F sites at the interface; this structure was used to calculate the DOS and was obtained from the transformation of i-BLSi in the *ab initio* MD simulation and the subsequent quenching process. (b) Decomposed DOS for Si, Ca, and F in the w-BLSi displayed in (a). (c) Plot of multiplication of the Kubelka–Munk function and energy as a function of energy for CaSi₂F₁.₈–₂.₃ consisting of w-BLSi, trilayer silicene with dangling bonds, and F-terminated trilayer silicenes.
3.4 Exfoliation of layered silicon compounds

3.4.1 Exfoliation of CaSi₂

The formula of CaSi₂ including the formal charges is Ca²⁺(Si⁻)₂. Thus, the electrostatic interactions between the Ca²⁺ and Si⁻ layers are strong. However, it is very important to decrease the amount of negative charge on the silicon layers to facilitate exfoliation. With this aim, Mg-doped CaSi₂ is used as a starting material to decrease the interaction strength between the Ca and Si layers. Thus, the immersion of bulk CaSi₁.₈₅Mg₀.₁₅ in a solution of propylamine hydrochloride (PA·HCl) leads to deintercalation of the calcium ions, which is accompanied by the evolution of hydrogen (Figure 3.8a). CaSi₁.₈₅Mg₀.₁₅ is subsequently converted into a mixture of Mg-doped SiNS and an insoluble black metallic solid. A light brown suspension containing SiNS can be separated after the sediment is removed from the bottom (Figure 3.8b). Using X-ray photoelectron spectroscopy (XPS), the composition of the as-obtained SiNS is determined to be Si:Mg:O in a ratio of 7.0:1.3:7.5. The Si:Mg ratio is appreciably lower in the starting material CaSi₁.₈₅Mg₀.₁₅, thereby indicating that exfoliation into individual SiNS occurs preferentially in the section of the silicon layer where magnesium atoms are present.

The dimensions of the SiNS can be directly determined by atomic force microscopy (AFM), and the sheets are found to be 0.37 nm thick, with lateral dimensions ranging from 200 to 500 nm (Figure 3.8c and d). The crystallographic thickness of SiNS (0.16 nm) is calculated from its atomic architecture, and the
difference between this value and that obtained by AFM indicates that the surface of the SiNS is stabilized via capping with oxygen atoms as shown in Figure 3.8e. As revealed by the high-resolution AFM images, the closest distance between atoms (i.e., dot-like marks in the AFM image) is 0.41 ± 0.02 nm (Figure 3.8f), which is slightly larger than the distance between Si atoms in the Si(111) plane of bulk crystalline silicon (0.38 nm). These sheets are considered to be very similar to silicene. The overall exfoliation reaction comprised the following steps: (1) The oxidation of CaSi$_{1.85}$Mg$_{0.15}$ is initiated by the oxidation of the Ca atoms with PA·HCl, which is accompanied by the release of PA; (2) The resulting Mg-doped Si$_6$H$_6$ is likely very reactive and thus easily oxidized with water to form gaseous hydrogen; (3) Mg-doped layered silicon with capping oxygen atoms is exfoliated by reaction with the aqueous PA solution, thereby resulting in a stable colloidal suspension of SiNS.

The absorption spectrum of the silicon sheets shows a peak at 268 nm (4.8 eV), corresponding to the L→L critical point in the silicon band structure, which is strongly blue shifted with respect to the bulk indirect band gap of 1.1 eV (Figure 3.9). The absorbance at 268 nm is observed to be linearly dependent on the silicon content and excludes a possible association of nanosheets in this concentration range (Figure 3.9, inset). The photoluminescence (PL) spectrum obtained using an excitation wavelength of 350 nm shows an emission peak at 434 nm (2.9 eV). These results directly indicate that the 2D silicon backbone is maintained, since the PL spectra of the silicon quantum dots with diameters lower than 2 nm show a peak at 3 eV that red shift by as much as 1 eV upon exposure to oxygen. Moreover, the absence of PL from defect or trap-state recombination, which typically occurs near 600 nm, supports the hypothesis that the observed PL is produced by direct electron–hole recombination in the silicon sheets, as occurs in silicon nanocrystals. As shown above, the exfoliation of Mg-doped CaSi$_2$ with PA·HCl results in SiNS with capping oxygen atoms.

### 3.4.2 LAYERED SILICON COMPOUNDS

Deintercalation of calcium from the interlayer of CaSi$_2$ can be achieved using HCl solutions at low temperatures (Figure 3.10). Thus, CaSi$_2$ changes into amorphous silica with the evolution of significant amounts of hydrogen upon reaction with a 1N HCl solution at room temperature. Treatment with ice-cold concentrated aqueous HCl resulted in CaSi$_2$ being topotactically transformed into a green-yellow solid (i.e., layered siloxene [Si$_n$H$_3$(OH)$_3$]) with the release of hydrogen gas, as described in Reaction (3.1):

$$3\text{CaSi}_2 + 6\text{HCl} + 3\text{H}_2\text{O} \rightarrow \text{Si}_n\text{H}_3(\text{OH})_3 + 3\text{CaCl}_2 + 3\text{H}_2$$

![Figure 3.9](image-url) Room-temperature optical properties of Mg-doped SiNS. UV/Vis spectra of SiNS suspensions at various concentrations. Inset: the absorbance at 268 nm was plotted against the concentration of SiNS.
The crystalline sheets contain puckered 2D Si layers similar to crystalline Si(111) layers, with Si atoms being stabilized by terminal hydrogen or hydroxide groups located out of the layer plane. At temperatures below −30°C, CaSi$_2$ is transformed into layered polysilane (Si$_6$H$_6$) without the release of hydrogen, as shown in Reaction (3.2). This means that additional reactions between the Si layer and water do not occur.

$$\text{3CaSi}_2 + 6\text{HCl} \rightarrow \text{Si}_6\text{H}_6 + 3\text{CaCl}_2$$ (3.2)

When compared with CaSi$_2$, the interlayer bonding between adjacent 2D Si layers is weaker in both Si$_6$H$_3$(OH)$_3$ and Si$_6$H$_6$ since the bonding takes place by weak hydrogen bonds and van der Waals forces, respectively. Using a solution of HCl in methanol, ethanol, butanol, C$_{12}$H$_{25}$, benzyl alcohol, or CH$_2$COOMe, the corresponding alkoxide-terminated organosiloxenes (Si$_6$H$_5$OR, where R = methanol, ethanol, butanol, C$_{12}$H$_{25}$, benzyl alcohol, or CH$_2$COOMe) can also be obtained. However, the organosiloxenes are insoluble in any organic solvent and hence do not exfoliate.

### 3.5 FUNCTIONALIZED SILICON NANOSHEETS

The chemical modification–exfoliation process provides a generic approach for preparing organo-chapped silicenes. In this method, layered polysilane (Si$_6$H$_6$) was used as a starting layered silicon compound with $sp^3$ silicon bonding. The hydrosilyl (Si-H) groups on the surface of Si$_6$H$_6$ are polarized as Si$^+\cdot$H$^-\cdot$ owing to the lower electronegativity of silicon compared with hydrogen, and can thus be utilized as a reaction point for the chemical modification of silicenes. The reactivity of the Si-H groups has been widely studied in the field of silicon chemistry and various methods for chemically modifying these groups have been developed. Thus, several chemically modified SiNS were successfully synthesized by reacting Si$_6$H$_6$ with various chemicals such as Grignard reagent (Sugiyama et al. 2010), hydrosilanes (Nakano et al. 2012), alkyl- or aryl-amines (Okamoto et al. 2015; Ohshita et al. 2016), metallic lithium (Ohashi et al. 2014), and ionic liquids (Nakano et al. 2014), as summarized in Figure 3.11.

#### 3.5.1 SYNTHESIS AND CHARACTERIZATIONS OF Ph-SiNS

The Grignard reaction is one of the important organometallic chemical reactions for C–C and C–Si bond formation (Ashish et al. 1996). In this reaction, aryl-magnesium halides (i.e., Grignard reagents) serve as...
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nucleophiles and react with the electrophilic atoms. Thus, phenyl-modified SiNS (Ph-SiNS) was successfully synthesized by the reaction of Si₆H₆ with phenyl magnesium bromide (Ph-MgBr) in tetrahydrofuran (Sugiyama et al. 2010). Halogenation of the silicon substrates is generally required for Si–C bond formation using Grignard reagents owing to the low reactivity of the Si-H group (Dahn et al. 1993). However, in the case of Si₆H₆, the Si-H groups react with Grignard reagents without halogenation. The as-obtained Ph-SiNS is a colorless paste that dissolves in typical organic solvents. FTIR and ¹H-NMR analyses indicate that the composition of Ph-SiNS is Si₆H₄Ph₂, thereby revealing the substitution of approximately 30% of the Si-H groups with phenyl groups. The XANES spectrum of this material exhibits two peaks at 1841 and 1844 eV, attributed to the Si–Si and Si–C bonds, respectively, with no peak derived from Si–O bonds being observed.

The AFM images of Si₆H₄Ph₂ show a flexible and flat-plane monolayer sheet with 1.11 nm thickness, which is in good agreement with the thickness value of the structural model of Ph-SiNS (Figure 3.12a through c). In addition, atomically resolved AFM images show a periodic arrangement of phenyl groups on the sheet surface as atom-like dots on the Si₆H₄Ph₂ surface (Figure 3.12d). The closest distance between the dots is 0.96 nm, which is in good agreement with the distance between phenyl groups in the Si₆H₄Ph₂ structural model (Figure 3.12e and f).

3.5.2 OPTICAL PROPERTIES OF AMINO-MODIFIED SiNS

An aryl-methyl moiety, having photoelectric characteristics, can also be attached to the surface of Si₆H₆. Amino-modified SiNS surfaces treated with benzene- (Ph-), naphthalene- (Np-), and carbazole- (Cz-) containing amino substituents are prepared by dehydrogenative coupling of Si₆H₆ with the corresponding amines (Ohshita et al. 2016). XRD analysis of the obtained samples reveals a clear diffraction peak at 1.32 nm for Np-SiNS, which is likely ascribed to the stacked structure. In contrast, no clear XRD peaks are observed for Ph-SiNS and NS-SiNS. This is indicative of the strong tendency of Np-SiNS to form stacking structures, likely originating from the extended conjugation of naphthalene.

The obtained samples exhibit different optical characteristics depending on the nature of the aromatic unit. Thus, UV/V absorption and PL bands produced by both the aromatic units and the SiNS consisting of 2D silicon frameworks are observed in each sample. The strong stacking nature of Np-SiNS is also confirmed from the PL spectrum, which shows a broad band likely ascribed to π stacking. Furthermore, photoinduced currents are observed for the Np-SiNS and Cz-SiNS films, which are prepared on the electrode by a drop-drying method (Figure 3.13). The photocurrent is generated by UV light irradiation, thereby suggesting that the aromatic substituents and/or silicon frameworks absorb the light for photocurrent generation.
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Figure 3.12 (a) AFM image of Ph-SiNS. (b) Line profile along the black line in (a). (c) Side view of the model structure of Ph-SiNS. (d) Atomically resolved AFM image of the surface of Ph-SiNS. (e) Line profile along the black line in (d). (f) Top view of the model structure of Ph-SiNS.

Figure 3.13 Photoinduced current generation behaviors of (a) naphthalene- (Np-) and (b) carbazole- (Cz-) modified SiNS films.
3.5.3 SELF-STACKING PROPERTIES OF AMINO-MODIFIED SiNS

The dehydrogenative coupling reaction can be widely applied to other organoamines for synthesizing other alkyl- or aryl-modified SiNS. Thus, other primary \( n \)-alkylamines, such as \( n \)-butyl- (C4-), \( n \)-hexyl- (C6-), \( n \)-decyl- (C10-), \( n \)-dodecyl- (C12-), and \( n \)-hexadecyl- (C16-) amines, also react with Si\(_6\)H\(_6\) to produce the corresponding alkylamine-modified SiNS (Okamoto et al. 2015). The XRD peak attributed to the stacking structure, namely (001) planes, shifts to lower angles depending on the length of the alkyl chain and the interlayer distance [calculated from the (001) reflection] and expands to 1.3–3.35 nm (Figure 3.14a). This result indicates that the interlayer distance can be controlled by the length of the attached alkyl chains. The linear proportional relation between the interlayer distance (\( d \) spacing) of the obtained samples and the carbon number of the \( n \)-alkylamine suggests that the attached \( n \)-alkylamines are regularly arrayed, taking the same conformation. The slope of 0.172 nm suggests a bilayered alkyl chain structure at a tilt angle of ca. 47° with respect to the stacking layers (Figure 3.14b and c).

The reaction of Si\(_6\)H\(_6\) with \( \alpha \), \( \omega \)-alkyldiamines, except for diaminopropane, readily progressed to produce alkyldiamine-modified SiNS (Okamoto et al. 2015). Even in this case, the interlayer distance expands depending on the length of the alkyl chain, but the degree of expansion of the interlayer distance is lower than that of \( n \)-alkylamine-derived SiNS. Since both ends of amino groups in the alkyldiamines react with the SiNS, a single-layer structure of alkyldiamine is formed in the interlayer space. The relationship between the interlayer distance and the carbon number in the alkyldiamine suggests a single-layered alkyldiamine structure at a tilt angle of ca. 66° with respect to the stacking layers (Figure 3.15a and b). In addition, the alkyldiamine-modified SiNS shows a low dispersibility against organic solvents, since the SiNS layers should be covalently bonded by the alkyldiamines.

By using alkyamine derivatives such as \( \omega \)-aminocarboxylic acids, novel functional groups can be introduced on the SiNS surface via the alkyl chains. Thus, 12-aminododecanoic acid (C\(_{12}\)COOH) reacted with Si\(_6\)H\(_6\) in pyridine to form a carboxylic group-containing alkyl chain fixed on the SiNS surface by Si–N linkages (Okamoto et al. 2015). The XRD pattern indicates that the interlayer distance of 12-aminododecanoic acid-modified SiNS (C\(_{12}\)COOH-SiNSs) is approximately half that of \( n \)-dodecylamine-modified SiNS. This result implies that C\(_{12}\)COOH moieties attached to adjacent silicon layers mutually overlap each other (Figure 3.15c). The introduction of carboxylic groups on SiNS via alkyldiamine-linkage creates new possibilities for the development of applications such as combinations with other types of layered materials.

3.5.4 THEORETICAL PROPERTIES

Theoretical studies of SiNS, such as DFT or tight-binding calculations, can be used to explore possible stable 2D structures of Si, which are often modeled by considering graphene analogs of Si. DFT and \textit{ab initio} MD simulations were used to investigate the properties of single-layer organo-modified SiNS [Si\(_6\)H\(_4\)Ph\(_2\)]. The calculations can be performed within the framework of DFT using the projector-augmented wave method and the generalized gradient approximation using the exchange–correlation functional PBE as implemented in the Vienna \textit{ab initio} simulation package.

The optimized structure of the organo-modified SiNS obtained from DFT calculations is presented in Figure 3.16a. The structure is stable, and the model structure for the Si\(_6\)H\(_4\)Ph\(_2\) nanosheet is highly plausible, because each of the phenyl groups can easily rotate and tilt at 300 K. The band structure (Figure 3.16b) shows that the organo-modified nanosheet has a direct band gap of 1.92 eV, which represents a widened band gap compared with that of bulk Si (0.7 eV) calculated using the same computational parameters. It is interesting to note that the hydrogenated Si single-layer nanosheet shows a comparable indirect band gap of ca. 2 eV, while the Si\(_6\)H\(_4\)Ph\(_2\) nanosheet shows a direct band gap of ca. 2 eV, thereby demonstrating the significant effect of molecular functionalization (or doubling the thickness of the hydrogenated nanosheet) on its electronic structure.

The total EDOSs is presented in Figure 3.16c through f along with the partial orbital-decomposed EDOS for Si, C, and H atoms. The major contribution to the bands at and just below the highest occupied level is from the Si 2\( p_x \) and 2\( p_y \) states (Figure 3.16d), which would involve bonding...
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Figure 3.14 (a) XRD patterns of \( n \)-alkylamine-modified SiNS having different lengths of alkyl chain. (b) Relationship between the \( d \) space and \( m \) for \( C_m \)-SiNS stacked structures. Peaks marked with circles are derived from the (001) plane of \( C_m \)-HCl salts. (c) Structure model of regularly stacked \( C_6 \)-SiNS.

Figure 3.15 (a) Relationship between the \( d \) space and \( m \) for Di\( C_m \)-SiNS stacked structures. (b) Structure model of Di\( C_{12} \)-SiNS. (c) Approximate structure model of \( C_{12} \)COOH-SiNS.
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between Si atoms of the nanosheet. In contrast, the main contribution to the conduction band is from the C $2p_x$ and $2p_y$ orbitals (Figure 3.16e). The deeper valence states, between ca. 4 and 10 eV below the highest occupied level, are primarily comprised of Si $s$ states, with minor contributions from the C orbitals. The H $s$ bands (Figure 3.16f) are generally coincident with the C $p_x$, $p_y$, and $p_z$ bands, as expected from their bonding in the phenyl groups. In addition, the overlap of the H $s$ and Si $p_z$ states, primarily between 2 and 4 eV, indicates the formation of strong Si–H bonds, as indicated by the electron localization function (ELF) plot. Overall, the spiky profile of the CDOS indicates a weak electronic interaction between these atoms, which is also suggested by the band structure and the ELF profile.

3.5.5 ELECTRICAL PROPERTIES OF LITHIATED SiNS

Apart from the abovementioned methods, the Si-H groups present on the Si$_6$H$_6$ surface can be modified by mechanochemical solid-phase reaction (Ohashi et al. 2014). Thus, lithiated SiNS (Li-SiNS) were synthesized by mechanical kneading of Si$_6$H$_6$ with metallic lithium (Li) using an agate mortar (Figure 3.17a). This mechanochemical lithiation of Si$_6$H$_6$ proceeded at room temperature under an argon atmosphere with the release of hydrogen gas, with Li-SiNS being obtained as a homogeneous powder after kneading for 30 min (Figure 3.17b). The substitution rate of the Si-H groups with Li is controlled by the additive amount of metallic lithium. Thus, Li-SiNS having different lithium content (Si$_6$H$_6$–$n$Li$_n$) can be prepared (Figure 3.17c).

FTIR measurements indicate that the intensity of the Si–H stretching vibration at 2100 cm$^{-1}$ is reduced in accordance with the rate of lithiation, while the Si–Li stretching vibration is confirmed at 450 cm$^{-1}$ (Figure 3.18a). XANES measurements also support the formation of Si–Li bonds. XRD measurements reveal typical diffraction peaks of Si$_6$H$_6$, with layered ((001) and (002) planes) and hexagonal crystal structures of the Si framework ((100) and (110) planes) changing, depending on the extent of the lithiation process. In addition, no diffraction peak attributed to Li metal is observed in the lithiated samples. These results reveal the distortion of the Si framework and the collapse of the layered structure upon lithiation. The electron band structure of Si$_6$H$_6$ is also changed as a result of the lithiation process. As shown in Figure 3.18b, the diffuse reflection absorption spectra of Si$_6$H$_6$–$n$Li$_n$ reveal a shifting of the absorption band edge of Si$_6$H$_6$–$n$Li$_n$ to longer wavelengths while showing lower band gap energies (0.85 eV) compared with Si$_6$H$_6$ (2.2 eV). The completely lithiated sample (Si$_6$Li$_6$) shows semiconductor-like conductivity values.
Silicene and SiNS are additional examples of 2D novel materials beyond graphene. When compared with graphene, they have some differences (since the sheets are puckered), such as the point-group symmetry and pseudospin. Thus, these materials are predicted to have Dirac cones similar to graphene but with a larger spin-orbital gap and with a band gap opening under a perpendicular electric field. Their physical properties are generally less extreme compared with graphene (e.g., slightly lower mechanical strengths and electron Fermi velocities), although they can present better physical properties, such as thermoelectric figure of merit and a richer topological phase diagram.
Currently, freestanding silicene (i.e., without functional groups) has not been achieved experimentally. Nevertheless, there is a strong resemblance between the organo-modified SiNS reviewed in this text and the predicted freestanding silicene. Therefore, knowledge of the properties of SiNS is a good starting point for understanding the properties of silicene on a substrate or on a functionalized material. Finally, on-demand molecular design and control of the surface modification of 2D silicon nanomaterials are key processes for developing electric devices and energy storage materials in the near future. 2D silicon materials could trigger a revolution in the semiconductor industry to achieve the ultimate in miniaturization if they could be used to build electronic devices.

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REFERENCES


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