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Chemical Synthesis of Silicon Nanosheets from layered calcium disilicide

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Abstract. The synthesis of silicon nanosheets (SiNSs) without using conventional vacuum processes and vapor deposition is challenging and is anticipated to receive significant attention for a wide range of applications. Thereby, mass production of silicon nanosheets with low cost can be achieved using top-down approach starting from materials including a 2D sheet structure as a fundamental unit. We have recently, developed a soft synthetic method for the preparation of silicon sheets in gram-scale quantities by redox-assisted chemical exfoliation (RACE) of calcium disilicide (CaSi2). In this review, we will present chemical methods for the synthesis and modification of silicon sheets.

1. Introduction

Low-dimensional nanomaterials are of particular interest as they may exhibit anisotropic and/or dimension-tunable properties, both of which are important attributes for nanodevice applications [1].

The silicon photovoltaic property discovered, two decades ago, by Canhamin in porous Si has not only challenged bulk semiconductor band structure models but also significantly expanded the potential applications of the Si-based materials [2,3]. The nanoscale properties of materials with nanometer dimensions differ from those of the bulk one. Nanostructured silicon materials compared to the bulk silicon materials exhibit photovoltaic effects, ballistic electron emission, much lower thermal conductivity and higher chemical activities. These properties lead to excellent potential application in photovoltaic cells, nonvolatile memory, lighting, ultrasonic generators, biosensors and other applications. Zero-dimensional (0D) crystalline Si, such as Si nanoparticles (SiNPs)[4,5] and one-dimensional (1D) nanomaterials, such as Si nanowires SiNWs [6,7] and Si nanotubes (SiNTs)[8,9] have been synthesized. The fabrication techniques have been intensively studied to improve size and chemical stability, as well as to achieve high yield. Silicon Nano-sheets (SiNSs), a low dimensional crystalline silicon materials with their high specific surface area, makes them promising candidates for a variety of applications in nanoscience and nanotechnology. There are two prominent types of SiNSs:

- buckled sheet mainly based on the Si (111) structure, with the same honeycomb lattice structure, but is corrugated due to sp³ hybridization.
- silicene with a graphene-like honeycomb lattice structure and a mixed sp³-sp² hybridization, that is weakly corrugated [10].
Many types of nanosheets that consist of oxidized substrates, such as silicate layers or metal oxides, have been reported. However, buckled Si sheets or silicene have not been extensively developed.

Before addressing chemical synthesis methods of silicon sheets, a comparison of chemical and physical properties of silicon with those of carbon are first briefly outlined in table 1. More details can be found in several reviews and books [16-18].

Silicon and Carbon are in Group 14 of the periodic table. They have four electrons in the outermost shell, four valence orbitals which lead to formation of four two-electron covalent bonds. However, there are many differences between these two elements in terms of their structural, chemical and physical properties. These differences affect the ability for formation of their respective nanomaterials and nanostructures.

<table>
<thead>
<tr>
<th>Carbon</th>
<th>Silicon</th>
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<tbody>
<tr>
<td>Group 14 in the periodic table</td>
<td>Group 14 in the periodic table</td>
</tr>
<tr>
<td>four electrons in the outermost shell</td>
<td>four electrons in the outermost shell</td>
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<tr>
<td>four valence orbitals</td>
<td>four valence orbitals</td>
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<tr>
<td>formation of four two-electron covalent bonds</td>
<td>formation of four two-electron covalent bonds</td>
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<tr>
<td>Paulings electronegativity $\chi$ 2.55 for C and 2.20 for H</td>
<td>lower electronegativity $\chi = 1.90$</td>
</tr>
<tr>
<td>polarization of the C-H bond $C^{\delta-} - H^{\delta+}$</td>
<td>opposite sense polarization $Si^{\delta+} - H^{\delta-}$</td>
</tr>
<tr>
<td>C-H bonds are rather strong</td>
<td>Si-H more reactive</td>
</tr>
<tr>
<td>the valence s and p orbitals with large energy difference (10.60 eV) giving rise to sp, sp$^2$, and sp$^3$ hybridizations</td>
<td>smaller energy difference between the s and p orbitals (5.66 eV), lower hybridization energies. Silicon tends to use all its three p orbitals, resulting in sp$^3$ hybridization</td>
</tr>
<tr>
<td>no energetically accessible d orbitals to expand its coordination or valence shell</td>
<td>d orbitals (or other virtual orbitals) are energetically low-lying allowing silicon to expand its coordination sphere from four to five or six.</td>
</tr>
<tr>
<td>small atomic size means efficient $\pi-\pi$ overlap and the formation of stable double and triple bonds C-C, C=C, and C≡C bond lengths are 1.54, 1.34, and 1.20Å</td>
<td>larger atomic size of silicon results in poor $\pi-\pi$ overlaps</td>
</tr>
<tr>
<td>C=C 1.54Å result in planar structures</td>
<td>Si-Si and Si=Si bonds length of 2.35 and 2.16Å.</td>
</tr>
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</table>

Stable crystalline silicon typically assumes only the sp$^3$ hybridization system and favors a tetrahedral diamond-like structure. Silicon equivalent of graphene was first mentioned in a theoretical study by Takeda and Shiraishi in 1994 [19] and then reinvestigated by other groups,
who named it silicene [20-23]. Silicene with a honeycomb graphene-like structure has been observed recently by scanning tunneling microscopy (STM) on Ag(110) and on Ag(111) surfaces [24,25,26]. Silicene formation has also been studied on Au(110) [27], Ir(111) [28] and on ZrB$_2$ [29] surfaces. So far, these silicon structures have been grown using epitaxial growth techniques under UHV. However, silicene does not seem to exist in nature and there is no solid phase silicon similar to graphite. This is inconsistent with theoretical studies that have predicted the stability of silicene nanosheets inserted into a graphite-like lattice, such as ultrathin AlN stacks [30] or modified lattice structures through incorporation of transition-metal ions (M=Ti, Nb, Ta, Cr, Mo, and W) to form MSi$_2$ [31]. Zintl phases metal disilicides that incorporate rare-earth metals and alkaline earth metals, MSi$_2$ (M=Yb, Er,Tm, Lu and Ca), have graphite-like, stacked 2D silicon sub-network structures that are isomorphous with AlB$_2$ [32]. Such binary compounds are synthesized by direct reaction between the metal and silicon in a helium atmosphere at $T > 900^\circ$C [33]. Topochemical transformation of layered Zintl phases can be used to obtain sheet polymers. Nevertheless, the exact stoichiometry of the polymers obtained and their properties depend on the specific reactions taking place.

Recently, we have developed a soft synthetic method for silicon sheets, with hexagonal graphitic-like structure resembling that of silicene, in gram-scale quantities by redox-assisted chemical exfoliation (RACE) of calcium disilicide (CaSi$_2$) [34].

This review focuses on chemical synthesis and modification of silicon sheets. We shall begin by topochemical reactions of layered Zintl phases in section 2 with the well-known reactions of CaSi$_2$ investigated more recently. A brief structural discussion of calcium disilicide (CaSi$_2$) that includes 2D silicon puckered will be introduced. The Preparation of SiNSs by surface modification of Si$_6$H$_6$ will be presented in section 3. Finally, our conclusions and future plans for silicon sheet will be presented in section 4.

2. Synthesis of SiNSs by topochemical reactions of the layered Zintl phases

The top-down solution approach is recently a reliable way to synthesize SiNSs by using materials including a 2D sheet structure as a fundamental unit.

Alkali and alkaline earth silicides belong to the family of Zintl phases, in which polyanionic species, formed of the tetrelide [35] atoms counter balance the electropositive metal cations [36-38]. These compounds are interesting because the Si atom occur with negative oxidation states and low coordination numbers, and they form unusual low-dimensional structures such as sheets, chains or isolated polyhedra. They are also important precursors for the synthesis of bulk amorphous semiconductors, including Si nanoparticles prepared by solution-phase routes or in the solid state [39] and also the expanded framework solids known as semiconductor clathrates that are isomorphous with ice clathrate hydrates [40-42]. Among the Zintl silicides, only calcium disilicide (CaSi$_2$) has a structure of interconnected Si$_6$ rings forming anionic 2D silicon puckered sheets (Si$_2$)$_{2n}$ held together by Ca$^{2+}$ that form planar monolayers (Figure 1). The covalent structure of the silicide layers is stable and remarkably flexible [43-45] and can be chemically modified by oxidation, leading to removal of the intercalated metal ions.

2.1. CaSi$_2$ as precursor material for the preparation of silicone nanosheets

Removal of Ca$^{2+}$ from CaSi$_2$ has been achieved by Bonitz et al. [46] during treatment of a suspension of CaSi$_2$ in CCl$_4$ with gaseous Cl$_2$ (eq. 1).

$$ (CaSi_2)_n + nCl_2 \rightarrow (Si)_2n + nCaCl_2 $$

The 2D silicon sheets obtained according to equation (1) is unstable, highly reactive, and cannot be easily handled and characterized.[47, 48]

In 1863, Whler reported for the first time the synthesis of stable siloxene sheet polymer (Si$_6$H$_3$(OH)$_3$) by topochemical transformation of CaSi$_2$ in ice-cold aqueous HCl solution as a
Figure 1. (a) Crystal structure of CaSi$_2$ (cell parameters: $a=3.855$ Å and $c=30.60$ Å with space group $R \overline{3} m$). The large circles represent Ca atoms and the small circles represent Si atoms. (b) Silicon sheet in CaSi$_2$ crystal structure. (c) Weiss siloxene Si$_6$H$_3$(OH)$_3$. All OH groups are replaced to H atoms in layered polysilane Si$_6$H$_6$.

yellow compound called "Silicon" (eq. 2). During this transformation, Ca$^{2+}$ ions are removed without destroying the polyanion layers, which then forms the backbone of the resulting sheet polymer.

$$3CaSi_2 + 6HCl + 3H_2O \rightarrow Si_6H_3OH_3 + 3CaCl_2 + 3H_2$$  \hspace{1cm} (2)

Kautsky later modified the reaction conditions and obtained a gray-green amorphous product "siloxene" [50]. This material is of considerable interest due to its intense luminescence and the possibility of shifting the luminescence wavelength through substitution [51, 52].

Weiss et al. in 1979 [45] proposed that the crystalline sheet polymer structure was a puckered Si 2D layers similar to crystalline Si(111) layers stabilized though termination of hydrogen or hydroxide groups pointing out of the layer plane. This suggestion was later confirmed by Dahn et al. (Figure 1) [53]. The use of a solution of HCl in methanol or ethanol instead of an aqueous solution led to the preparation of alkoxide-terminated siloxenes (Si$_6$H$_3$(OCH$_3$)$_3$ or Si$_6$H$_3$(OC$_2$H$_5$)$_3$) (eq. 3). [54]

$$3CaSi_2 + 6HCl + 3ROH \rightarrow Si_6H_3(RO)_3 + 3CaCl_2 + 3H_2$$  \hspace{1cm} (3)

R= methyle, ethyle

The treatment at temperatures below -30°C resulted in non-oxidized silicon sheet polymer; a layered polysilane (Si$_6$ H$_6$), with similar structure to Si$_6$H$_3$OH$_3$, but in which Si atoms are terminated by hydrogen (Figure 1) (eq. 4) [55, 56].

$$3CaSi_2 + 6HCl \rightarrow Si_6H_6 + 3CaCl_2$$  \hspace{1cm} (4)

Performing the reaction at 0°C, Dahn et al. obtained the same layered polysilane Si$_6$ H$_6$ [53]. However, Yamanaka et al. reported formation of Si$_6$H$_3$OH$_3$ as by-product which was then removed by washing with a solution of HF [55].
During topochemical transformation, CaSi$_2$ was spontaneously cleaved to yield siloxene platelets by reactive deposition epitaxy (RDE) method.\cite{49}

Layered siloxene Si$_6$H$_3$(OH)$_3$ was successfully exfoliated into individual nanosheets with a thickness of 0.7 nm and lengths in the range 100-200 nm by Nakano et al. \cite{57}, using sodium dodecyl sulfate as dispersant agent (Figure 2). Sodium dodecylsulfate (SDS) and thin plate-like crystals of Si$_6$H$_3$(OH)$_3$ were shaken at room temperature for 10 days, to give a translucent colloidal suspension. The suspension remained stable for two months without precipitation. This can be used to synthesize Si$_6$H$_3$(OH)$_3$ nanosheets, but the silicon skeleton is partially oxidized.

**Figure 2.** a) TEM image of Si$_6$H$_3$(OH)$_3$ nanosheets. b) Electron diffraction pattern for the Si$_6$H$_3$(OH)$_3$. Indices and spacings for the diffraction rings 10 and 0.313 nm (ring 1), 11 and 0.188 nm (ring 2), and 20 and 0.163 nm (ring 3), respectively. c) Schematic illustration of the Si$_6$H$_3$(OH)$_3$ nanosheet. Reproduced from reference \cite{57}.

### 2.2. Synthesis from Mg-doped CaSi$_2$ (CaSi$_{1.85}$Mg$_{0.15}$)

One of the most important techniques to exfoliate single layers from their parent layered compound is the adjustment of the charge on the silicon layer in CaSi$_2$. To weaken the electrostatic interaction between the Ca$^{2+}$ and ($Si_2$)$_\infty^{2-}$ layers, in CaSi$_2$, it is important to reduce the charge on the negatively charged silicon layers. For that, Nakano et al. \cite{58} have chosen Magnesium ($Mg^{2+}$) as electro-positive element to reduce silicon charge in CaSi$_2$. Mg-doped CaSi$_2$, (CaSi$_{1.85}$Mg$_{0.15}$) was prepared and used as a precursor for the chemical synthesis of silicon sheets. They prepared CaSi$_{1.85}$Mg$_{0.15}$ by melting a mixture of CaSi, Si, and Mg; then the material obtained was treated in a solution of propylamine hydrochloride (PAHCl), resulting in the de-intercalation of Ca$^{2+}$ ions and the formation of a light-brown suspension containing silicon nanosheets (SiNSs). The following mechanism for the exfoliation process was proposed: 1) oxidation of CaSi$_{1.85}$Mg$_{0.15}$ with PAHCl, accompanied by the liberation of PA; 2) the presumably very reactive Mg-doped Si$_6$H$_6$ obtained is readily oxidized by water to form gaseous hydrogen; and 3) Mg-doped layered silicon with capping oxygen atoms is exfoliated by reaction with the aqueous solution of PA.

TEM image (Figure 3) revealed a 2D structure with lateral dimensions in the range of 200 to 500 nm. The composition of the obtained monolayer SiNSs was determined to be...
Si/Mg/O = 7.0:1.3:7.5 by X-ray photoelectron spectroscopy (XPS). Monolayer and ultrathin sheets were evidenced by Atomic force microscopy (AFM) (Figure 3) with an average thickness of 0.37 nm measured at intervals between the sheets and the substrate surface.

The Electron Diffraction pattern (Figure 3) confirmed that the sheet was single crystalline and the diffraction spots could be indexed as hk reflections of a hexagonal lattice with a = 0.82 nm, which corresponds to approximately twice of the interplanar distance of the (111) planes of bulk silicon (0.38 nm). Therefore, the exfoliation of Mg-doped CaSi$_2$ using PAHCl produces less than 1% of surface-oxidized silicon nanosheets (SiNSs). This oxygen capping is inherent to the process, because the capping is thought to promote exfoliation when the layered silicon becomes a stable colloidal suspension by reaction with aqueous propylamine solution. Despite these studies, the chemical synthesis of pure silicon sheets has not yet been reported.

Figure 3. a) TEM image of the sheet. b) ED pattern recorded along the [001] zone axis perpendicular to the surface of the sheet. C) Noncontact mode AFM image of the silicon sheets. Reproduced from reference [58]

2.3. Redox assisted chemical exfoliation of CaSi$_2$

Direct chemical synthesis of pure silicon sheets in gram-scale quantities has been recently reported by our group using redox-assisted chemical exfoliation (RACE) of potassium modified calcium disilicide (CaSi$_2$).[34] Let us recall that CaSi$_2$ is an ionic (Ca$^{2+}$(Si$_2$)$_2$$^{-2}$) material, and the reduction of the charge on the (negatively charged) silicon layers is an important step in order to weaken the electrostatic interaction between the Ca$^{2+}$ and (Si$_2$)$_2$$^{-2}$ layers.[58] For that, we have chosen potassium (K) as doping element with low melting point (63.2°C), high reactivity and lower electronegativity. We proposed the following mechanism for the exfoliation process:

1) Diffusion of potassium (K) in CaSi$_2$ at 160 °C, leads to formation of the K$_{2x}$Ca$_{1-x}$Si$_{2-x}$ phase and a small amount of KSi and Ca metal driven by the reduction of some Ca$^{2+}$ by K, as shown in the following chemical equation (5):

$$CaSi_2 + 3xK \rightarrow K_{2x}Ca_{1-x}Si_{2-x} + xKSi + xCa$$

(5)

(2) The obtained mixture was then treated with a degassed solution of isopropylamine hydrochloride (i-PAHCl) in ethanol at room temperature for 24 hours under nitrogen. The calcium ions are deintercalated accompanied by the evolution of hydrogen (eq. (6)) and a greenish-brown suspension was formed accompanied with an insoluble black solid which was assigned to the unreacted CaSi$_2$ after confirmation by XRD study. The SiNSs was obtained
after filtration of the greenish-brown suspension in 20% yield. These steps can be summarized by the following three chemical equations:

$$K_{2x}Ca_{1-x}Si_{2-x} + 2iPA.HCl \rightarrow 2xKCl + (1 - x)CaCl_2 + (2 - x)Si(SNSs) + 2iPA + H_2 \quad (6)$$

It is important to note that when adding the iPA.HCl solution, a strong evolution of hydrogen is observed which may be due to excess potassium oxidation (eq. (8)). The rate of hydrogen evolution involving the oxidation of deintercalated calcium (eq. (7)) accompanied by liberation of nanosheets of silicon, decreases significantly after a few minutes.

$$Ca + 2iPA.HCl \rightarrow CaCl_2 + 2iPA + H_2 \quad (7)$$

The excess potassium reacts with iPA.HCl to release $H_2$ as follows:

$$K + iPA.HCl \rightarrow KCl + 2iPA + 1/2H_2 \quad (8)$$

The synthesized sheets were analyzed by X-ray photoemission spectroscopy (XPS), high-resolution transmission electron microscopy (HR-TEM) and energy dispersive X-ray spectroscopy (EDX) (Figure 4). XPS measurements show that the synthesized sheets contain almost exclusively Si atoms and displayed a Si 2p peak with a binding energy of 100 eV, which is different from that of SiO$_2$ (104 eV) (Figure 4a). Energy-dispersive X-ray spectroscopy (EDX) experiments show a small trace of oxygen which is due to exposure of the powder to air. HR-TEM experiments (Figure 4b) reveal that the synthesized silicon product consists of highly ordered stacked silicon sheets. Electron diffraction pattern (Figure 4d) shows hexagonal arrangement, consistent with well-ordered and crystalline silicon sheets.

![Figure 4](image_url)

**Figure 4.** a) XPS spectrum of the synthesized Si sheets, the Si 2p core levels shown, b) TEM image showing a stack of silicon sheets, c) TEM image showing a highly oriented crystalline silicon sheet, d) ED pattern recorded perpendicular to the surface of the sheet. Reproduced from reference [35]

This hexagonal pattern originates either from a quasi-two dimensional hexagonal lattice, with the observed spots corresponding to the four (100) and the two (110) reflections. From the
interplanar distance $d_{100}$ (or $d_{110}$), the 2D hexagonal lattice constant $a_{\text{hex}}$, was calculated to be $(0.330 \pm 0.018)\text{nm}$ which is smaller than the 0.38 nm corresponding to the (111) plane structure of bulk silicon. Therefore, these silicon sheets may correspond to a 2D honeycomb Si lattice stacked in planes with a surface lattice constant $a_{\text{hex}} = (0.330 \pm 0.018)\text{nm}$, corresponding to a distance between the first Si atoms neighbors of 0.19 nm. Previous studies reported that silicene is corrugated [25,28,10,59-61] with a buckling between 0.04 and 0.12 nm [62,63], resulting in a projected distance (in the plane of the hexagons) as low as 0.19 nm. The data clearly show that the synthesized Si sheets do not correspond to the (111) layer of Si diamond lattice; instead they have a hexagonal graphitic-like structure resembling that of silicene.

3. Preparation of SiNSs by surface modification of Si$_6$H$_6$

Capping of layered silicon compounds with organic groups rather than oxygen atoms is supposed to promote their exfoliation, and assist in the control of the interlayer spacing. Moreover, the synthesis of organically modified layered silicon allows for the preparation of carbon-coated silicon nanosheets by mild non-oxidative pyrolysis.

The introduction of organic groups on Si$_6$H$_6$ through $Si - C$ or $Si - N$ bonds is plausible method to obtain SiNSs capped with organic moieties, because of their high dispersion in organic solvents and their stability with respect to oxidation and/or hydrolysis, due to formation of hydrophobic surface on silicon. In contrast to carbon, silicon ($\chi = 1.90$) is less electronegative than hydrogen ($\chi = 2.20$); hence, Si-H bonds are polarized in the opposite sense, as $\text{Si}^6+\cdot \text{H}^0$. This implies that nucleophilic attacks on silanes usually occur at the silicon centers. Silanes are also much more reactive than the corresponding hydrocarbon analogues due to larger polarization. The high reactivity of silanes and hydride-terminated silicon crystalline surfaces are also due to weak $Si - H$ bonds, which are significantly weaker than $C - H$ bonds.

Based on this characteristic, layered polysilane, Si$_6$H$_6$, is a suitable starting material for the preparation of non-oxidative silicon nanosheets by organic modification and exfoliation. Si$_6$H$_6$ can be prepared from calcium disilicide (CaSi$_2$),[55,56] and each layer of Si$_6$H$_6$ consists of two-dimensional corrugated Si(111) planes, in which the Si$_6$ rings are interconnected and a H atom is bound to each Si atom in the direction perpendicular to the layer.[45,53,55]

3.1. Hydrosilylation reaction

Surface modification of silicon particles or substrates with organic groups, can be achieved through hydrosilylation of hydrogen-terminated silicon surface with unsaturated organic groups, such as alkenes and alkynes.[64a] However, this reaction did not proceed readily for Si$_6$H$_6$. Si-H bonds as reactive sites are not readily accessible because they are located in the interlayer spacing of the layered starting material. Therefore for the reaction to happen, it is imperative that the organic moiety must be intercalated into the interlayer. The reactivity of Si$_6$H$_6$ must be increased by halogenations;[64b] however, this is undesirable, because highly toxic gases such as PCl$_5$, CCl$_4$, or Cl$_2$ are required.

Recently, Nakano et al.[65] have functionalized Si$_6$H$_6$ with hexyl chains using a Pt-catalyzed hydrosilylation reaction with 1-hexene to produce a stable colloidal suspension (Scheme 1). The obtained product was soluble in typical organic solvents, such as hexane, chloroform, acetone, and ether, and insoluble in water and ethanol.

FTIR and Si K-edge X-ray absorption near-edge structure (XANES) analyses (Figure 5) revealed that the 1-hexene does not merely attach to Si$_6$H$_6$, but reacts with it to form Si-C linkages. The IR spectrum (Figure 5a) shows an alkyl stretching and bending absorptions bands between 2856 and 2954 cm$^{-1}$ and between 1259 and 1459 cm$^{-1}$, respectively. In addition, a band attributable to $Si - CH_2$ vibrational scissoring was observed at 729 cm$^{-1}$. The presence of characteristic vibrations for organic molecules in the sheets after the reaction, along with a reduction in the intensity of $Si - H$ at 2110 cm$^{-1}$ and the absence of bands characteristic of a
Scheme 1: Hydrosilylation of Si₆H₆ with 1-hexene catalyzed by platinum.

Terminal double bond ($C = C$; 1600 cm⁻¹), indicate that the organic molecules were covalently attached to silicon surface. However, Si – O stretching vibrations bands observed between 1000 and 1100 cm⁻¹ indicate that the synthesized sheets were partially oxidized. XANES of prepared silicon sheet (Figure 5b) exhibits features at an energy of 1844 eV, which is intermediate between those measured for Si and SiO₂ samples. This peak was assigned to the Si – C bond, which is the same bond energy as that for a tetra-coordinated silicon atom-bonded organic group.[66a]

Figure 5. (a) FTIR spectra of [Si₆H₃(C₆H₁₃)$_3$]. (b) Si K-edge XANES spectra of [Si₆H₃(C₆H₁₃)$_3$] (brown line), Si(111) wafer and SiO₂ (black line). The data was recorded at BL-10 in the Ritsumeikan SR Center. (c) XPS Si 2p spectra of [Si₆H₃(C₆H₁₃)$_3$] (brown line), Si(111) wafer and SiO₂ (black line). (d) UV spectrum of [Si₆H₃(C₆H₁₃)$_3$]. Reproduced from reference [65]

The XPS spectrum displayed a Si 2p peak with a binding energy of 102.0 eV (Figure 5c), which is different from those of bulk Si (99.0 eV) and SiO₂ (104 eV). Compared to XPS data for decyl-capped silicon nanocrystals reported recently,[67] this binding energy (102.0 eV) was
attributed to a Si-organo group. AFM of the sheet gave a thickness of 3.1 nm (Figure 6), which was compared to thickness of 2.3 nm calculated from model structure optimized using force field mode in Discover program. The model structure was constructed on the basis of the ideal formula [Si$_6$H$_3$(C$_6$H$_{13}$)$_3$] (Scheme 1). The thickness indicated that the sample was composed of monolayer sheets.

Further results obtained by the authors, showed that the two-dimensional silicon sublattice is maintained in the prepared silicon sheet. From the XRD data, the authors suggested that the peak observed at 12.4$^\circ$ indicates molecular-scale periodicity of 0.71 nm, which consists of silicon-hexane composites. The same value (0.71 nm) was calculated from the proposed structural model (Figure 6c) for the periodicity of hexyl groups on the sheet surface. However this procedure leads to SiNSs with capping oxygen atoms. The sheet was stabilized through termination of hexane groups pointing out of the layer plane with (111) plane structure of bulk silicon since it was prepared from layered polysilane Si$_6$H$_6$.

### 3.2. Grignard reagent

Another method for the formation of Si-C bond in layered polysilane Si$_6$H$_6$ was recently reported by Sugiyama et al. The authors reported the synthesis of oxygen free, phenyl-modified organosilicon nanosheets with atomic thickness by the reaction of layered polysilane [Si$_6$H$_6$] with phenyl magnesium bromide [PhMgBr] (Scheme 2).

![Scheme 2: Reaction of Si$_6$H$_6$ with phenyl magnesium bromide [PhMgBr]](image)

The authors suggested that the phenyl group was successfully bonded to the silicon sublattice based on the fact that the material obtained as a colorless paste was soluble in typical organic solvents such as hexane, chloroform, acetone, or ether. The authors used FTIR and IH NMR spectroscopy to assign the formula Si$_6$H$_4$Ph$_2$ to the obtained SiNSs. The IR spectrum shows vibration bands at 1150 and 1410 cm$^{-1}$ corresponding...
to the Si-Ph bond and at 1700-2000 cm$^{-1}$ corresponding to aromatic C = C bond indicating that the organic molecules are covalently attached to the silicon surface. 1H NMR spectroscopy of Si$_6$H$_4$Ph$_2$ also supported results of IR spectroscopy, showing two resonances at 2.5-3.0 and 7.1-7.7 ppm corresponding to those of Si-H and Si-Ph, respectively.

XANES revealed two signals at 1841 and 1844 eV derived from Si-Si and Si-Ph bonds respectively. No signals of Si-O bonds were observed, even in measurements performed after storing the samples in air for one day [66]. The sheet was found to be stable toward oxidation and hydrolysis even with terminating hydrogen atoms on the surface, thus the material could be handled easily in air. Such increased stability of the material by the introduction of Si-C bonds is supported by previous reports on porous silicon[64a] and silicon nanowires (SiNWs).[67]

**Figure 7.** (a), AFM image of [Si$_6$H$_4$Ph$_2$] in contact mode. (b) Line profile along the black line in (a). (c) Side view of the model structure for [Si$_6$H$_4$Ph$_2$]. (d) Atomically resolved AFM image of the surface of [Si$_6$H$_4$Ph$_2$]. (e) Line profile along the black line in (d). (f) Top view of the model structure for [Si$_6$H$_4$Ph$_2$]. Reproduced from reference [66]

The photoluminescence spectrum of [Si$_6$H$_4$Ph$_2$] in 1,4-dioxane using excitation at 350 nm, shows a peak at 415 nm (3.0 eV) and in solid film shows four peaks at 415, 440, 465 (sh), and 505 nm (sh). The photoluminescence indicates the nature of the monolayer sheet, reflecting exfoliation into individual organosilicon nanosheets in an organic solvent and shows similar properties as one-dimensional polysilane.[68] Atomic force microscopy (AFM) and atomically resolved AFM revealed a completely flat plane surface and a periodic structure of the phenyl groups on the silicon surface (Figure 7). The thickness of the sheet was 1.11 nm which is close to the thickness (0.98 nm) calculated by using the force field in the program Discover on the basis of its atomic architecture (Figure 7c). Atomically resolved AFM images of an individual
sheet show an arrangement of atom-like dots on the top face with closest distance between the dots of \(0.96 \pm 0.02 \text{nm}\). The periodicity of phenyl groups on the model surface (Figure 7f), was estimated to be 1.0 nm, which is in good agreement with the closest distance between the dots in the AFM image. The approximate 1.0 nm periodicity was also confirmed by XRD.

3.3. Reaction with amine groups
Si atoms can easily accept nucleophilic attack of a lone pair from the amine N atoms because the Si-H bonds in \(\text{Si}_6\text{H}_6\) are similar to those in silyl hydride, that is, the bonds are polarized as \(\text{Si}^\delta^+ - \text{H}^\delta^-\). It is known that ammonia can be adsorbed on a Si surface and can then react with dangling bond sites without major disruption to the Si surface structure.\[69\] Formation of \(\text{Si} - \text{N}\) bonds upon reaction of n-alkylamines with chlorinated or hydrogenated Si surface have been reported.\[70-72\] Based on these studies, an approach to the synthesis of oxygen-free silicon nanosheets covered with amines using \(\text{Si}_6\text{H}_6\) as a starting material have been recently reported by Okamoto et al.\[73\] Reaction of \(\text{Si}_6\text{H}_6\) with n-Decylamine was monitored in chloroform at 60°C under nitrogen atmosphere for approximately 1 h (Scheme 3). Reaction progress is evidenced by a change in color and flotation of \(\text{Si}_6\text{H}_6\). A similar change was observed when n-butylamine was used instead of n-decylamine, but not for di- or tri-n-butylamine.\[73\] Bubble formation observed just after pouring the amine onto \(\text{Si}_6\text{H}_6\) implies that hydrogen is generated as a result of the reaction.

![Scheme 3: Proposed Reaction Scheme for the production of C_{10} - Si_n from Si_6H_6 and n-Decylamine][73].](#)

The authors suggested two possible outcomes concerning the binding mode in this surface modification; the amine either reacts with \(\text{Si}_6\text{H}_6\) or attaches to the surface of the silicon layers.\[73,74\] In the case of reaction (Scheme 3), some Si-H bonds react with amine molecules to form \(\text{Si} - \text{NH} - \text{R}\) linkages (R: decyl group) which subsequently react through its \(\text{N} - \text{H}\) bond with another \(\text{Si} - \text{H}\) bond on \(\text{Si}_6\text{H}_6\) to form a Si-NR-Si linkage. The final product contains both \(\text{Si} - \text{NH} - \text{R}\) and \(\text{Si} - \text{NR} - \text{Si}\) linkages in variable proportions, depending on the reaction conditions.

FTIR of the product (Figure 8) shows bands from 2800 to 3000 cm\(^{-1}\) and from 1350 to 1450 cm\(^{-1}\) attributed to the alkyl chain of n-decylamine. There is no band around 2100 cm\(^{-1}\), indicating \(\text{Si} - \text{H}\) stretching vibrations and no \(\text{N} - \text{H}\) stretching around 3300 cm\(^{-1}\). Asymmetric \(\text{Si} - \text{N} - \text{Si}\) stretching was also observed as weak peak at 930 cm\(^{-1}\).\[74\] These initial analyzes support the reaction procedure of the amine with \(\text{Si}_6\text{H}_6\) according to the proposed mechanism (Scheme 3).

XANES spectra (Figure 8) also revealed Si-N linkage in the layered polysilane and did not contain \(\text{Si} - \text{O}\) linkages. These results indicate that n-decylamine is not merely attached to
Si\textsubscript{6}H\textsubscript{6} but has actually reacted with Si\textsubscript{6}H\textsubscript{6}. Thermogravimetric analysis (TGA) of the product revealed that alkyl-chain moieties remained connected to the Si layers up to 400°C and suggested that the silicon layers in (C\textsubscript{10} – Si\textsubscript{n}) were densely covered with n-decylamine residues with an estimated ca. 0.7 mol of residue per mole of Si atoms in the reaction product.[73]

A small amount of C\textsubscript{10} – Si\textsubscript{n} is dispersible in chloroform and exfoliates to form SiNSs with lateral dimensions in the range of 12 nm, as shown by AFM (Figure 8d). SiNSs have flat and smooth surfaces, due to dense coverage of n-decylamine.[73] The thickness of the sheets was found to be 7.5 nm (Figure 8e) 10-20 times larger than that of a siloxene nanosheet [57] or than that of a Mg-doped silicon nanosheet [58] due to the long alkyl chains connected to the surface of the C\textsubscript{10} – Si\textsubscript{n} nanosheet on both sides.

Figure 8. (a) FTIR spectra of Si\textsubscript{6}H\textsubscript{6}, n-decylamine, and C\textsubscript{10} – Si\textsubscript{n}. The insets show enlarged spectra in the range from 800 to 1000 cm\textsuperscript{-1}. (b) Comparison of XANES spectra of C10-Sin with those of quartz, crystal silicon, and -Si\textsubscript{3}N\textsubscript{4} obtained using the TEY mode in a vacuum. (c) XRD pattern of C\textsubscript{10} – Si\textsubscript{n} in the agglomerated state. (d) AFM phase image of a C\textsubscript{10} – Si\textsubscript{n} nanosheet on a HOPG plate obtained in tapping mode. (e) Line profile measured along the white line denoted as (A) in panel a. Reproduced from reference [73]

XRD show peaks of puckered silicon sheets ((100) and (110) planes) with no peak corresponding to the (001) planes of Si\textsubscript{6}H\textsubscript{6}. This result indicates that Si\textsubscript{6}H\textsubscript{6} was transformed into C\textsubscript{10} – Si\textsubscript{n} through reaction with n-decylamine, and the crystalline sheet structure was preserved after the reaction. In the low-angle region a peak derived from (00l) planes appear with interlayer distance estimated to be 2.46 nm close to 2.54 nm, which is the expanded interlayer distance of siloxene due to intercalation of n-decylamine.[45]

The silicon sheets prepared by hydrosilylation, Grignard reaction or amination of Si\textsubscript{6}H\textsubscript{6} were stabilized though termination of organic groups pointing out of the layer plane with (111) plane structure of bulk silicon since they were prepared from layered polysilane (Si\textsubscript{6}H\textsubscript{6}).

4. Conclusions and Future Perspectives
Silicon-based nanotechnology is highly promising since it is compatible with conventional silicon microtechnology. The structural feature of silicon nanomaterials is their large specific surface areas, which are due to their size and shape on the nanometer scale. Here, we reviewed chemical synthesis methods of two dimensional silicon nanomaterials (SiNSs). We have described the developed soft synthetic method for the preparation of SiNSs by topochemical reaction of CaSi\textsubscript{2}, modified CaSi\textsubscript{2} and by the chemical surface modification of Si\textsubscript{6}H\textsubscript{6}. Stacked silicon layer scan
be exfoliated from CaSi$_2$ to provide SiNSs by using surfactants, compositional modification by Mg doping, and surface modification of Si$_6$H$_6$ with organic compounds using hydrosilylation, Grignard reaction and amination reaction. SiNSs maintain their characteristic 2D crystalline structure and stabilized through termination with organic groups pointing out of the layer plane with (111) plane structure of bulk silicon since they were prepared from layered polysilane (Si$_6$H$_6$).

Recently, we synthesized extended silicon sheets by simple room temperature procedure called redox assisted chemical exfoliation of calcium disilicide (CaSi$_2$). The data clearly show that the synthesized Si sheets do not correspond to the (111) oriented layers of Si diamond lattice; instead they have hexagonal graphitic-like structure resembling that of silicene. Silicon in the form of silicene may form a new avenue for an old player in the electronic industry, which may extend the lifetime of Moores law.

The application of this new synthetic approach is expected to be extended to the use of other systems and theoretical calculations should be performed to predict the product properties. SiNSs are expected to be developed for applications in various fields that can take advantage of their specific characteristics.

References

[41] Kautsky H 1921 Z. anorg. Chem. 117 209