Special Feature: Nanostructured Materials

Synthesis and Modification of Silicon Nanosheets

Hideyuki Nakano and Hirotaka Okamoto

Report received on July 6, 2011

■**ABSTRACT**‖　A variety of silicon nanosheets (SiNSs) and organo-modified SiNSs are reviewed. These nanosheets were prepared by a soft synthesis method and with chemical surface modification in a solution process. Application of organo-modification of the silicon nanosheets yielded a number of organosiloxene. Characterization revealed very high two-dimensional anisotropy for the obtained nanosheets, with a thickness of around 1 nm vs. a lateral size on the submicrometer scale. A multilayered film of organo modified SiNSs showed light-induced photocurrent, and restacked SiNSs were found to show high anode capacitance for lithium ion battery electrodes.

1. Introduction

Layered host compounds have been subjected to intensive research over the past decade. Once a layered compound is exfoliated into its elementary layers, the resulting individual layers are called nanosheets because their thickness is on the order of nanometers while their lateral dimensions are on the order of sub-micrometers to micrometers.[1] Several groups have synthesized a variety of nanosheets, including those of oxides,[2] niobates,[3] chalcogenides,[4] phosphates,[5] and the recently discovered graphene,[6] by delaminating the appropriate layered precursors. Some of these show attractive chemical and physical properties, such as size-quantization effects, which are associated with the unusual two-dimensional structural feature. Furthermore, nanosheets can be also be used as building blocks for novel supramolecular assemblies. Because nanosheets disperse in a solvent as molecular entities, they can be aggregated or assembled into a variety of organized nanostructures.

Based on previously reported methods, the delamination of layered silicon compounds is a reliable way to synthesize SiNSs if there are suitable two-dimensional (2D) Si structures. Layered silicon compounds, such as polysilane (Si_6H_6) and siloxene ($Si_6H_3(OH)_3$), are crystalline layered polymers formed by a backbone of puckered Si 2D layers similar to the (111) planes of the three-dimensional (3D) crystal Si. Although many researchers have attempted to prepare 2D silicon sheets, there are no reports of successful fabrication of such silicon nanosheets. This is because the individual layers strongly interact with each other, are not easily exfoliated, and cannot be dissolved in either organic or inorganic solvents. Recently, our group has succeeded in the synthesis of SiNSs by the exfoliation of Si_6H_6 and $Si_6H_3(OH)_3$ through organic modifications of the interlayer space.[7-11] This review mainly described our recent results for SiNSs, organo-modified SiNSs, and their potential as electronic devices.

2. Layered Silicon Compounds as a Starting Material

Figure 1 illustrates crystal structures of a layered silicon compound as a starting material of the SiNSs. Among the many Zintl silicides, calcium disilicide ($CaSi_2$) has a structure that includes 2D silicon puckered sheets in which the Si_6 rings are interconnected; the puckered $(Si^-)_n$ polyanion layers are separated from each other by planar monolayers of Ca^{2+} (Fig. 1(a)).

The covalent bonding of the silicon sub-networks of the Zintl silicides is very stable and versatile, and can be chemically modified by oxidation, i.e., by the removal of metal. Based on this, a siloxene sheet polymer ($Si_6H_3(OH)_3$) was formed by treating $CaSi_2$ with ice-cold concentrated aqueous HCl.[12] The $CaSi_2$ transformed into a green-yellow solid and hydrogen gas was released by the following reaction:

$$3CaSi_2 + 6HCl + 3H_2O \rightarrow Si_6H_3(OH)_3 + 3CaCl_2 + 3H_2$$
$$\cdots \cdots \cdots \cdots \cdots \cdots (1)$$
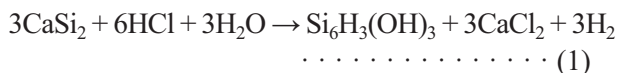
The structure of siloxene has been controversial. A crystalline sheet polymer structure with puckered Si 2D layers similar to crystalline Si(111) layers, which are stabilized though termination of hydrogen or hydroxide groups pointing out of the layer plane, was proposed by Weiss et al. in 1979,[13] and later confirmed by Dahn et al. (Fig. 1(b)).[14] Yamanaka et al. reported that treatment at temperatures below –30°C resulted in suppression of the oxidation yielding another Si sheet polymer, a layered polysilane (Si_6H_6), without the evolution of hydrogen.[15,16]

$$3CaSi_2 + 6HCl \rightarrow Si_6H_6 + 3CaCl_2 \cdots \cdots \cdots (2)$$
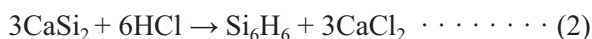
Si_6H_6 has a structure similar to that of $Si_6H_3(OH)_3$, but all Si atoms in Si_6H_6 are terminated by hydrogen and no oxygen atoms are included. The interlayer bonding between adjacent polymer sheets in $Si_6H_3(OH)_3$ and Si_6H_6 is weaker than that in $CaSi_2$ because it involves only weak contributions of van der Waals forces and hydrogen bonds (only for $Si_6H_3(OH)_3$) in the former. Recently, we synthesized several alkoxide-terminated organosiloxenes (Si_6H_5OR, R; Bu, $C_{12}H_{25}$, Bn, and CH_2COOMe)[11] according to the method reported by Weiss et al. Organic moieties that are longer or bulkier than methoxy and ethoxy groups expand the interlayer
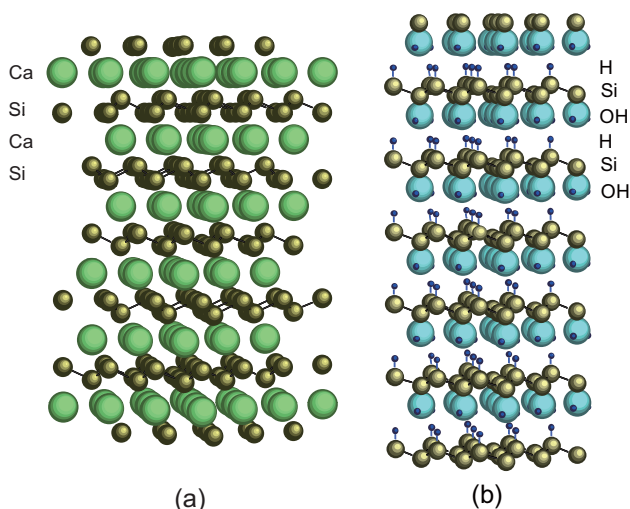
distance to a larger extent than those observed for $Si_6H_3(OCH_3)_3$ or $Si_6H_3(OC_2H_5)_3$.

3. Synthesis of Silicon Nanosheets

The first approach is to prepare nanosheets of $Si_6H_3(OH)_3$ using a surfactant.[7] Sodium dodecylsulfate ($C_{12}H_{25}OSO_3Na$) was added to thin plate-like crystals of $Si_6H_3(OH)_3$ and then shaken at room temperature for 10 days. This produced a translucent colloidal suspension that remained stable for 2 months without precipitation.

It is important to clarify and understand how the layered host compounds undergo exfoliation into single layers. **Figure 2** shows X-ray diffraction (XRD) patterns for the wet colloidal aggregate centrifuged from the suspension revealing that the parent siloxene was exfoliated into individual nanosheets, a small portion of which were stacked to provide small-angle scattering. Upon drying, almost all of the siloxene nanosheets were restacked as a 10-20 sheet unit with a basal spacing of 3.8 nm, which represents a large expansion from the original value of 0.63 nm for siloxene and can be identified as belonging to a
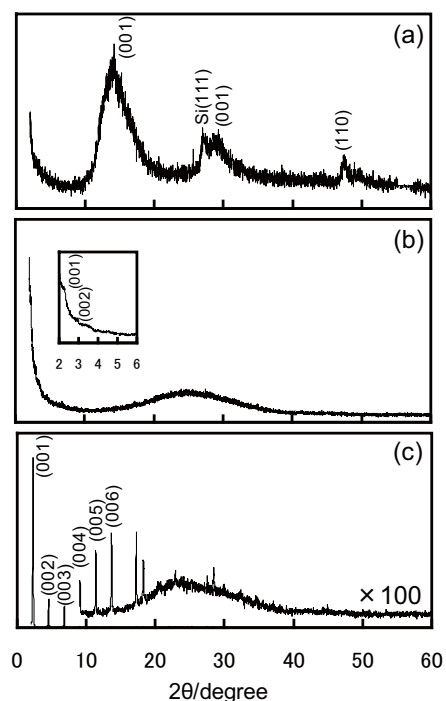
Fig. 2 XRD pattern before and after exfoliation of (a) a polycrystalline sample of $Si_6H_3(OH)_3$, (b) a wet colloidal aggregate, and (c) a dried colloidal aggregate centrifuged from the exfoliated $Si_6H_3(OH)_3$ suspension for 1 h at 30°C.

Fig. 1 Schematic illustration of (a) $CaSi_2$ and (b) Weiss siloxene, $Si_6H_3(OH)_3$ structures.

dodecylsulfate intercalated compound (Fig. 2(c)).

Another method employs Mg-doped $CaSi_2$ to reduce the interaction between Ca^{2+} and $(Si^-)_n$.[8] Mg-doped $CaSi_2$ ($CaSi_{1.85}Mg_{0.15}$) was successfully prepared by melting a stoichiometric mixture (Ca:Si:Mg = 1:1.85:0.15) of CaSi, Si, and Mg. Immersion of the bulk $CaSi_{1.85}Mg_{0.15}$ in a solution of propylamine hydrochloride (PA·HCl) led to deintercalation of the calcium ions accompanied by the evolution of hydrogen; $CaSi_{1.85}Mg_{0.15}$ was then converted into a mixture of SiNSs and an insoluble black metallic solid. A light-brown suspension containing SiNSs was obtained after the sediment was removed from the bottom of the flask. The overall exfoliation reaction comprises the following steps: 1) oxidation of $CaSi_{1.85}Mg_{0.15}$ initiated by the oxidation of Ca atoms with PA·HCl, accompanied by the liberation of PA; 2) the resulting Mg-doped Si_6H_6 is presumably 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 that results in a stable colloidal suspension of SiNSs. The composition of the monolayer SiNSs obtained was determined to be Si:Mg:O = 7.0:1.3:7.5 using X-ray photoelectron spectroscopy (XPS). The Si:Mg ratio is appreciably smaller in the $CaSi_{1.85}Mg_{0.15}$ starting material, which indicates that exfoliation into individual SiNSs occurred preferentially in a section of the silicon layer where magnesium atoms were present.

The formation of unilamellar nanosheets was confirmed by direct observations using transmission electron microscopy (TEM) and atomic force microscopy (AFM). The dispersed materials in the suspension were deposited onto various substrates or a TEM sample grid for the observations. **Figure 3** shows TEM and XRD for the sample from the layered silicide, $CaSi_{1.85}Mg_{0.15}$, as a typical example. A TEM image of the silicon sheets reveals a two-dimensional structure with lateral dimensions in the range of 200 to 500 nm (Fig. 3(a)). The ED pattern (Fig. 3(b)) confirmed that the sheet is single-crystalline and that the diffraction spots could be indexed as *hk* reflections of a hexagonal lattice with *a* = 0.82 nm, which corresponds to approximately twice the value of the (111) plane structure of bulk silicon (0.38 nm). XRD showed a peak corresponding to the (110) plane (Fig. 3(c)); however, the in-plane diffraction pattern of the silicon sheet could not be assigned to any siloxene structures. Thus, the SiNSs have a superlattice

structure with twice the period of the (111) plane structure of bulk silicon. The thickness of the sheets was 0.37 nm, as measured by AFM (**Figs. 4**(a) and (b)). The crystallographic thickness of the SiNS was calculated to be 0.16 nm on the basis of its atomic architecture. The difference between this value and that obtained by AFM indicates that the surface of the SiNS was stabilized by capping oxygen atoms. High-resolution AFM imaging revealed that the closest distance between the dot-like atoms in the AFM image is 0.41 ± 0.02 nm (Fig. 4(c)), which is slightly larger than the distance between the Si atoms in the Si(111) plane of the bulk crystalline silicon (0.38 nm). On the basis of the high-resolution AFM and TEM, it is considered that the sheet cores consist of a single-crystalline silicon monolayer with the thickness of a slightly squashed Si(111) plane.

4. Organo-modification of Silicon Nanosheets

The first attempt to synthesize organo-modified SiNSs was performed by exfoliation of amine-modified Si_6H_6.[9] The Si_6H_6 reacts with *n*-decylamine in chloroform by stirring at 60°C in a nitrogen atmosphere for approximately 1 h. Progress in the
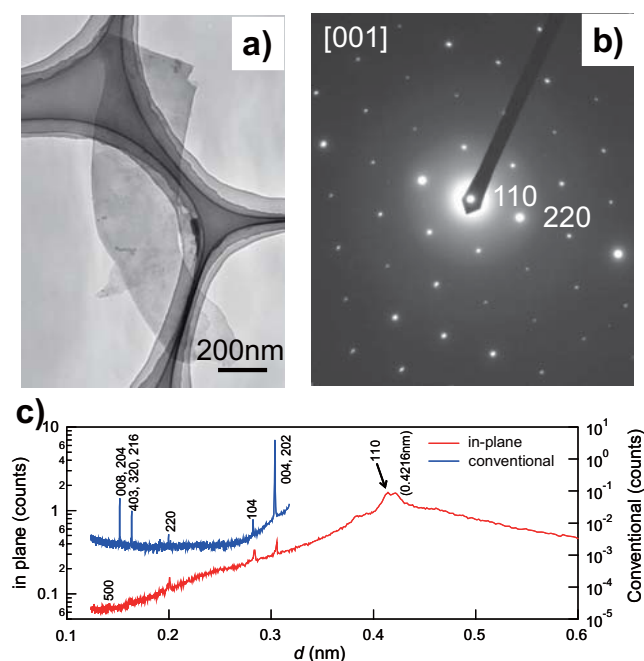

Fig. 3   (a) TEM image of a nanosheet. (b) The ED pattern recorded along the [001] zone axis perpendicular to the surface of the sheet. (c) In-plane XRD scans with an incident angle of 0.2˚ (red line) and conventional θ-2θ scan (blue line) of the sheet.

reaction was evidenced by a change in color and flotation of Si_6H_6, as shown in **Fig. 5**. A similar change was observed when *n*-butylamine was used instead of *n*-decylamine, but not for di-*n*-butylamine or tri-*n*-butylamine.

FTIR and Si K-edge X-ray absorption near-edge structure (XANES) analyses revealed that the *n*-decylamine does not merely attach to Si_6H_6, but reacts with it to form Si-N linkages. The XANES spectra also showed that the amine-modified Si_6H_6 did not contain Si-O linkages. The reaction of an amine with ≡Si-H corresponds to that of *n*-hexylamine and hydrogen terminated SiNPs.[17] It is thought that Si atoms can easily accept the nucleophilic attack of a lone pair from N atoms in the amine, because the Si-H bonds in Si_6H_6 are similar to silyl hydride, i.e., the bonds are polarized as $Si^{\delta+}$–$H^{\delta-}$. The *n*-decylamine-modified Si_6H_6 (C10-Si_n) is oxidized in air, but is thermally stable. Thermogravimetric analysis (TGA) and FTIR of the sample heated above 400°C revealed that alkyl chain moieties remain connected to the Si layers. The TGA results also suggest that the silicon layers in C10-Si_n are densely covered with *n*-decylamine residues and have few defects. A small amount of C10-Si_n is dispersible in chloroform solution and exfoliates to form SiNSs with lateral dimensions in the range of 1-2 μm, as shown by AFM (**Fig. 6**(a)).
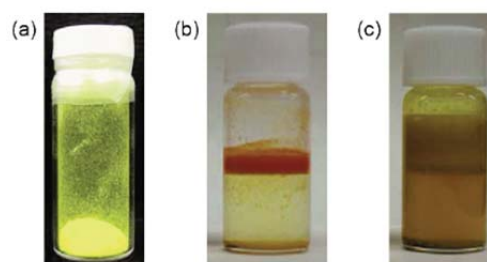

Fig. 5 Photographs of prepared samples of (a) layered polysilane (Si_6H_6), (b) Si_6H_6 reacted with *n*-decylamine (C10-Si_n) for 12 h in chloroform at 60°C in a nitrogen atmosphere, and (c) after heating at 120°C for ca. 24 h.
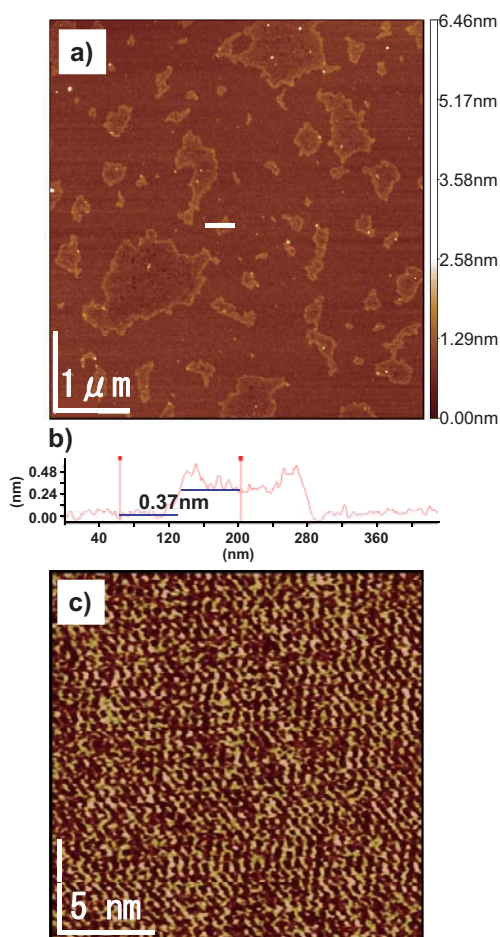

Fig. 4 (a) Noncontact mode AFM image of the nanosheet. (b) Line profile taken along the white line in (a). (c) Atomically resolved AFM image of the nanosheet.
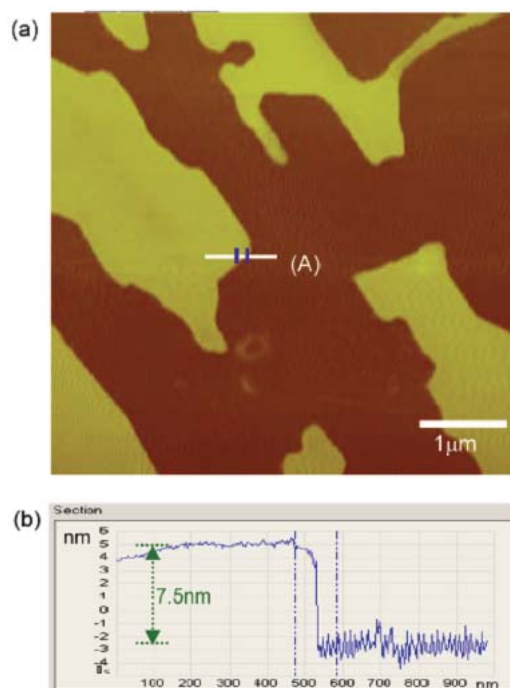

Fig. 6 (a) AFM phase image of a C10-Si_n nanosheet on a HOPG plane obtained in the tarring mode. (b) Line profile measured along the white line denoted as (A) in panel (a).

The SiNSs have very flat and smooth surfaces, due to the dense coverage of *n*-decylamine, with a thickness of 7.5 nm (Fig. 6(b)). The thickness of this nanosheet is 10-20 times larger than that of the siloxene nanosheet or the Mg-doped SiNS, due to the long alkyl chains on the surface as well as incomplete exfoliation (two or three stacked layers). It seems to be difficult to obtain a monolayer structure, because C10-Si$_n$ and other amine-modified nanosheets have a strong tendency to stack when they are dried from solution.

Spectrophotometric measurements of dilute C10-Si$_n$ solutions reflect the characteristics of the nanosheet structure. UV-vis absorption spectra for the solutions were characterized by Lambert–Beer behavior and exhibited a peak at 276 nm with a shoulder around 283 nm, which is very close to that for the siloxene nanosheet (ca. 300 nm), and the Mg-doped silicon nanosheet (268 nm). Moreover, the absorption edge of the C10-Si$_n$ solution at approximately 380 nm corresponds to that of the network polysilynes (360-390 nm).[18-20] A broad main peak appears at 438 nm (2.8 eV) in the PL spectrum obtained using an excitation wavelength of 350 nm. The peak positions are mostly the same as those for the Mg-doped silicon nanosheet or a silicon network polymer with hexyl side chains. The bandgap energy and broadness of the PL spectra reflect the structure of the two-dimensional silicon nanomaterials.

The introduction of organic groups on Si$_6$H$_6$ through Si-C bonds is another plausible method to obtain SiNSs capped with organic moieties. After numerous unsuccessful trials, phenyl-terminated SiNSs (Si$_6$H$_4$Ph$_2$) were successfully synthesized by the reaction of Si$_6$H$_6$ with phenyl magnesium bromide (PhMgBr).[10] An intermediate halogenation step is usually required for the introduction of organic groups using a Grignard reagent on bulk Si(111), due to the low reactivity;[21] however, the synthesis of SiNSs was successfully achieved without this step. The material obtained is a colorless paste and is soluble in typical organic solvents such as hexane, chloroform, acetone, or ether. FTIR and ^{1}H nuclear magnetic resonance (NMR) revealed that Si$_6$H$_4$Ph$_2$ includes not only Si-Ph bonds, but also Si-H bonds. ^{1}H NMR also indicated approximately twice as many of the Si-H bonds compared to the Si-Ph bonds. XANES revealed two peaks derived from Si-Si and Si-Ph bonds, although no features related to Si-O bonds were evident, even in measurements performed after storing the samples in air for 1 day. Si$_6$H$_4$Ph$_2$ was found to be stable toward oxidation and hydrolysis, even with terminating

hydrogen atoms on the surface, and thus the material could be easily handled in an air atmosphere. Such increased stability of the material by the introduction of Si-C bonds is supported by previous reports on porous silicon[22] and SiNWs.[23] The PL emission of Si$_6$H$_4$Ph$_2$ in 1,4-dioxane using 350 nm excitation provided a peak at 415 nm, which is almost the same as other SiNSs. AFM of Si$_6$H$_4$Ph$_2$ revealed a completely flat plane surface with a sheet thickness of 1.11 nm (**Figs. 7** (a) and (b)), which is close to the thickness (0.98 nm) calculated using the force field in the program Discover${}^®$ on the basis of its atomic architecture (Fig. 7(c)). The thickness and flatness of the Si$_6$H$_4$Ph$_2$ surface indicated that the sample was composed of monolayer sheets. Interestingly, the sample had the shape of a band with a folded moiety and was very thin and flexible, similar to silk. Atomically resolved AFM revealed a periodic structure of the phenyl groups as atom-like dots on the silicon surface (Fig. 7(d)). The closest distance between the dots was measured to be 0.96 ± 0.02 nm (Fig. 7(e)). The periodicity of phenyl groups on the Si$_6$H$_4$Ph$_2$
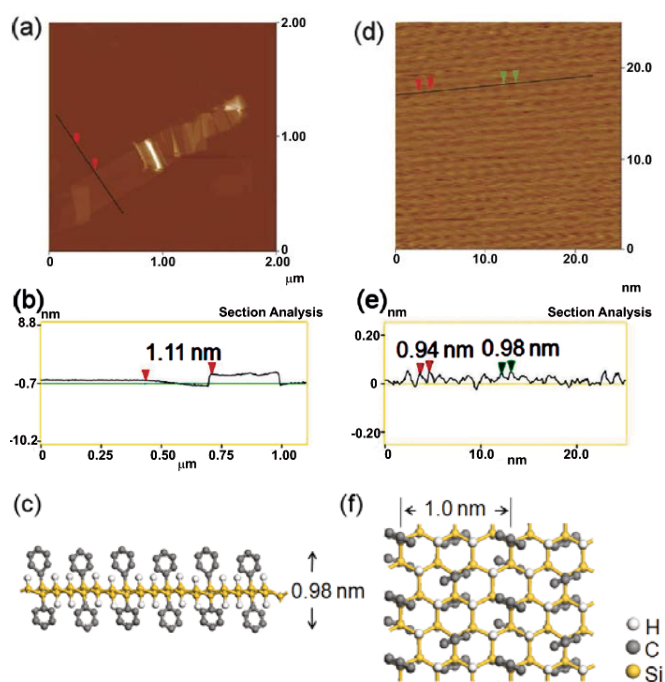

Fig. 7   (a) AFM image of [Si$_6$H$_4$Ph$_2$] in contact mode.
(b) Line profile along the black line in (a).
(c) Side view of the model structure of [Si$_6$H$_4$Ph$_2$].
(d) Atomically resolved AFM image of the surface of [Si$_6$H$_4$Ph$_2$].
(e) Line profile along the black line in (d).
(f) Top view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

structural model was estimated to be 1.0 nm (Fig. 7(f)), which is in good agreement with the closest distance between the dots in the AFM image.

5. Potential Applications

SiNSs are expected to be developed for various applications in electronic and photonic devices, and as lithium ion battery electrodes. Interestingly, light-induced photocurrent in the $Si_6H_4Ph_2$ film was observed under direct irradiation from a xenon lamp, which disappeared when the irradiation was cut off using a shutter (**Fig. 8**). When a filter was used to cut off wavelengths less than 420 nm, no photocurrent was observed. The photocurrent thus exhibited wavelength-dependence for the irradiated light, which indicated that the origin of the photocurrent is a bandgap transition. The results from this study are very significant, considering that there has been no previous report on photocurrent generation in polysilynes.

Silicon nanomaterials have also been expected to find application as lithium ion battery anodes to increase the energy density. Silicon is known to form lithium alloys, and when Li-Si alloys are electrochemically formed the maximum theoretical capacity is approximately 4200 mAh/g, which is much higher than that of the conventionally employed carbonaceous materials (372 mAh/g).[24-26] However, silicon anodes suffer from a large change in volume during the charge-discharge cycles, which leads to cracking and pulverization of the silicon particles and results in significant capacity fade. A composite involving silicon nanomaterials is a plausible solution to this problem, by minimizing the dimensional
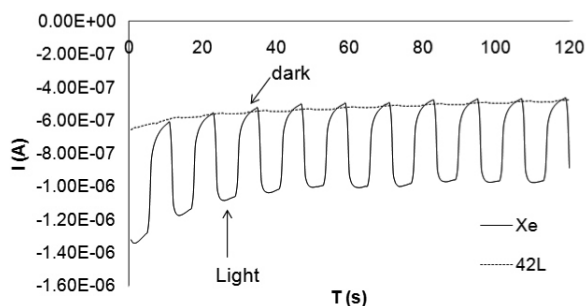
changes and failure of Li alloy electrodes during cycling by pulverization.[26-30] The advantage of SiNSs was exemplified with their use as an electrode fabricated directly by Vapor-Liquid-Solid (VLS) or vapor-solid methods. SiNSs are also a candidate anode material, due to their dimensional features. The electrical capacitance of and structural changes in SiNSs were examined by our group, and the electrode of SiNSs has higher capacitance (1620 mAh/g) and a smaller change in volume than the Si powder electrode during the lithium insertion and deinsertion process.[31]

6. Conclusions

We have developed a soft synthesis method for SiNSs by the chemical modification of layered silicon compounds. SiNSs maintain their characteristic 2D crystalline structure and exhibit PL characteristics related to the structure. Phenyl capped SiNSs also exhibit light-induced photocurrent under direct irradiation with UV light. It is expected that this new synthetic approach will be developed by employing various techniques, and theoretical calculations need to be performed to predict the properties. SiNSs have extraordinarily high specific surface areas and can be used as building blocks for the fabrication of devices by solution processes.

Fig. 8　Light-induced photocurrent in the [$Si_6H_4Ph_2$] film. The solid line (Xe) indicates photocurrent in the sample with direct irradiation, and the dotted line (42L) indicates photocurrent with irradiated light with wavelength greater than 410 nm obtained using a filter.

References

(1) Schaak, R. E. and Mallouk, T. E., *Chem. Mater.*, Vol.14 (2002), pp.1455-1471.

(2) Sasaki, T., *J. Ceram. Soc. Jpn.*, Vol.115 (2007), pp.9-16.

(3) Miyamoto, N., Yamamoto, H., Kaito, R. and Kuroda, K., *Chem. Commun.*, No.20 (2002), pp.2378-2379.

(4) Yang, D., Sandoval, S. J., Divigalpitiya, W. M. R., Irwin, J. C. and Frindt, R. F., *Phys. Rev. B*, Vol.43 (1991), pp.12053-12056.

(5) Alberti, G., Cavalaglio, S., Dionigi, C. and Marmottini, F., *Langmuir*, Vol.16 (2000), pp.7663-7668.

(6) Novoselov, K. S., Geim, A. K., Morozov, S. V., Jiang, D., Zhang, Y., Dubonos, S. V., Grigorieva, I. V. and Firsov, A. A., *Science*, Vol.306 (2005), pp.666-669.

(7) Nakano, H., Ishii, M. and Nakamura, H., *Chem. Commun.*, No.23 (2005), pp.2945-2947.

(8) Nakano, H., Mitsuoka, T., Harada, M., Horibuchi, K., Nozaki, H., Takahashi, N., Nonaka, T., Seno, Y. and Nakamura, H., *Angew. Chem. Int. Ed.*, Vol.45 (2006), pp.6303-6306.

(9) Okamoto, H., Kumai, Y., Sugiyama, Y., Mitsuoka, T.,

Nakanishi, K., Ohta, T., Nozaki, H., Yamaguchi, S., Shirai, S. and Nakano, H., *J. Am. Chem. Soc.*, Vol.132, No.8 (2010), pp.2710-2718.

(10) Sugiyama, Y., Okamoto, H., Mitsuoka, T., Morikawa, T., Nakanishi, K., Ohta, T. and Nakano, H., *J. Am. Chem. Soc.*, Vol.132, No.17 (2010), pp.5946-5947.

(11) Sugiyama, Y., Okamoto, H. and Nakano, H., *Chem. Lett.*, Vol.39 (2010), pp.938-939.

(12) Brandt, M. S., Vogg, G. and Stutzmann, M., *Silicon Chemistry (Eds: Jutzi, P. and Schubert, U.)*, (2003), pp.194-213, Wiley-VCH, Weinheim.

(13) Weiss, A., Beil, G. and Meyer, H., *Z. Naturforsch.*, Vol.34b (1979), pp.25-30.

(14) Dahn, J. R., Way, B. M., Fuller, E. and Tse, J. S., *Phys. Rev. B*, Vol.48 (1993), pp.17872-17877.

(15) Yamanaka, S., Matsu-ura, H. and Ishikawa, M., *Mater. Res. Bull.*, Vol.31 (1996), pp.307-316.

(16) Nishimura, K., Nagao, Y., Yamanaka, S. and Matsu-ura, H., *Jpn. J. Appl. Phys.*, Vol.35 (1996), pp.L293-L296.

(17) Liao, Y. C. and Roberts, J. T., *J. Am. Chem. Soc.*, Vol.128 (2006), pp.9061-9065.

(18) Bianconi, P. A. and Weidman, T. W., *J. Am. Chem. Soc.*, Vol.110 (1988), pp.2342-2344.

(19) Bianconi, P. A., Schilling, F. C. and Weidman, T. W., *Macromolecules*, Vol.22 (1989), pp.1697-1704.

(20) Furukawa, K., Fujino, M. and Matsumoto, N., *Macromolecules*, Vol.23 (1990), pp.3423-3426.

(21) Bansal, A., Li, X., Yi, S. I., Weinberg, W. H. and Lewis, N. S., *J. Phys. Chem. B*, Vol.105 (2001), pp.10266-10277.

(22) Buriak, J. M., *Chem. Rev.*, Vol.102 (2002), pp.1271-1308.

(23) Haick, H., Hurley, P. T., Hochbaum, A. I., Yang, P. and Lewis, N. S., *J. Am. Chem. Soc.*, Vol.128 (2006), pp.8990-8991.

(24) Sharma, R. A. and Seefurth, R. N., *J. Electrochem. Soc.*, Vol.123 (1976), pp.1763-1768.

(25) Komaba, S., Mikami, F., Itabashi, T., Baba, M., Ueno, T. and Kumagai, N., *Bull. Chem. Soc. Jpn.*, Vol.79 (2006), pp.154-162.

(26) Yoshio, M., Wang, H., Fukuda, K., Umeno, T., Dimov, N. and Ogumi, Z., *J. Electrochem. Soc.*, Vol.149 (2002), pp.A1598-A1603.

(27) Besenhard, J. O., Yang, J. and Winter, M., *J. Power Sources*, Vol.68 (1997), pp.87-90.

(28) Lee, J. K., Smith, K. B., Hayner, C. M. and Kung, H. H., *Chem. Commun.*, Vol.46 (2010), pp.1428-1430.

(29) Chou, S. L., Wang, J. Z., Choucair, M., Liu, H. K., Stride, J. A. and Dou, S. X., *Electrochem. Commun.*, Vol.12 (2010), pp.303-306.

(30) Chan, C. K., Peng, H., Liu, G., McIlwrath, K., Zhang, X. F., Huggins, R. A. and Cui, Y., *Nat. Nanotechnol.*, Vol.3 (2008), pp.31-35.

(31) Kumai, Y., Shirai, S., Sudo, E., Seki, J., Okamoto, H., Sugiyama, Y. and Nakano, H., *J. Power Sources*, Vol.196 (2011), pp.1503-1507.

Hideyuki Nakano
  Research Fields:
    - Silicon Layered Structured Compounds
    - Silicon Nanosheets
    - Soft Chemical Synthesis
  Academic Degree: Dr. Eng.
  Academic Societies:
    - The Ceramics Society of Japan
    - The Chemical Society of Japan
  Award:
    - The Study Prize for Encouragement from the Ceramics Society of Japan Electronic Division, 2002

Hirotaka Okamoto
  Research Fields:
    - Nanocomposite Materials
    - Polymer Blends
    - Reactive Processing
  Academic Degree: Dr. Eng.
  Academic Societies:
    - The Society of Polymer Science, Japan
    - The Society of Rheology, Japan
    - The Society of Rubber Industry, Japan
  Awards:
    - The Best Paper Award from the Society of Rubber Industry, Japan, 2000
    - Nikkei Green Technology Award, 2002
    - SPSJ Award for Outstanding Achievement in Polymer Science and Technology, 2008