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Preparation of Alkyl-Modified Silicon Nanosheets by Hydrosilylation of Layered Polysilane (Si_6H_6)

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Supporting Information

ABSTRACT: Alkyl-modified crystalline silicon nanosheets **2** were synthesized and maintained the crystal structure of a Si(111) plane, in which the dangling silicon bond is stabilized by capping with the alkyl group. **2** was characterized using UV−vis, Fourier transform-infrared, and X-ray photoelectron spectroscopies; X-ray diffraction; and X-ray absorption near edge structure analysis. A model structure is proposed that has a periodicity through the nanosheet surface.

Techniques for the exfoliation of layered compounds are widely used to fabricate nanometer-thick materials, such as oxides,[1] niobates,[2] chalcogenides,[3] phosphates,[4] and the recently discovered graphene.[5] Although a variety of nanosheets have been synthesized, there have been few reports on silicon nanosheets (Si-NSs). The reaction of trihalosilane with an alkali metal was thought to be a plausible build-up method for the synthesis of Si-NSs. Bianconi et al. revealed that the products were amorphous bridged polysilane and/or silicon clusters.[6] As a result, it is very difficult to control the structural conformation of the products with this method. On the other hand, we have previously attempted to prepare Si-NSs through the chemical exfoliation of layered silicon compounds such as $CaSi_2$[7] and Si_6H_6.[8] The results have indicated that layered polysilane is a candidate starting material for the preparation of organo-modified Si-NSs.[9] Takeda et al. investigated the electron structure of one-dimensional (1D) and two-dimensional (2D) Si-skeleton materials. They indicated that the 2D material has a unique band structure, which is an intermediary between direct (1D) and indirect (3D).[10] The structure and photoluminescence properties of the layered silicon compounds were investigated by Stutzmann et al..[11] From these previous works, Si-NSs are believed to represent a different form of framework material with physical characteristics contrasting those of the more conventional bulk, thin-film, and nanocrystalline[12] forms. Recently, there is a need to expand the potential applications of such materials (for example, catalysis, batteries and sensors), and thus, we aim to develop a variety of functional Si-NSs according to the required application. The hydrosilylation reaction of the hydrogenated silicon substrate or silicon nanoparticle can progress under suitable conditions.[13] Therefore, we have focused on hydrosilylation for the preparation of functional Si-NSs, because among the various methods used to prepare functionalized silicon surfaces, hydrosilylation produces high quality, densely packed organic monolayers under relatively mild reaction conditions and provides excellent stability against oxidation. However, in the case of a layered silicon compound as the starting material, it would be difficult to modify the silicon surface because Si−H bonds as reaction points exist in the interlayer of the starting material. Therefore, one of the most important techniques to progress the reaction is that the catalysis and organo moiety must be intercalated into the interlayer.

In this study, we attempted to prepare **2** through hydrosilylation of layered polysilane (Si_6H_6) **1**. **1** was determined to have H-terminated Si(111) layers, stacked to form a graphite-like crystal, and the in-plane hexagonal silicon sublattice constant coincides with that of the Si(111) plane in the diamond structure (hexagonal setting Si(111); a = 0.385 nm), which indicates that the two-dimensional silicon network is preserved.[14]

1 was prepared according to the method described by Yamanaka et al.[15] Approximately 1 g of selected $CaSi_2$ crystallites with 5 mm^2 faces was immersed in 100 mL of 37% HCl at −30 °C. The mixture was stirred continuously for 5 days under an Ar atmosphere. The synthesized **1** was rinsed in dilute HF solution and then dried under vacuum at 110 °C. The resulting **1** (Figure 1a) was functionalized with hexyl chains using a Pt-catalyzed hydrosilylation reaction with 1-hexene to produce a stable colloidal suspension (Figure 1b). The obtained **2** is soluble in typical organic solvents, such as hexane, chloroform, acetone, and ether, and insoluble in water and ethanol.

Fourier transform-infrared (FT-IR) spectroscopy was used to identify and characterize the organic species on the silicon surface. Figure 2a shows the attenuated total reflection (ATR) IR spectrum for **2** after hydrosilylation with 1-hexene. The spectrum of **1** exhibited Si−OH, Si−H, and Si-OR stretching peaks at around 3400, 2110, and 1030 cm^{-1}, respectively, and a Si−H_2 bending peak at 914 cm^{-1}. On the other hand, the

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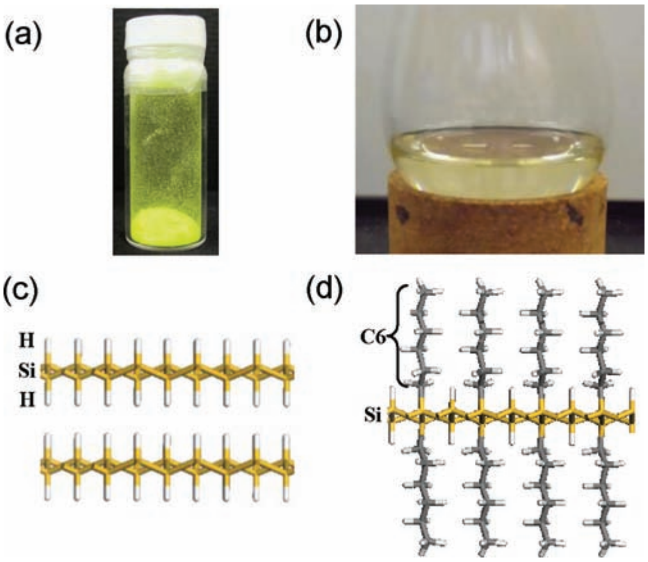

Figure 1. (a) Image and (c) structure of **1**. (b) Image and (d) structure of **2**.

spectrum after hydrosilylation contained alkyl stretching and bending absorptions between 2856 and 2954 cm^{-1} and between 1259 and 1459 cm^{-1}, respectively. In addition, a peak attributable to Si–CH_2 vibrational scissoring was observed at 729 cm^{-1}. The presence of characteristic vibrations for organic molecules in **2** after the reaction, along with a reduction in the intensity of Si–H at 2110 cm^{-1} and the absence of peaks characteristic of a terminal double bond (C=C; 1600 cm^{-1}), indicates that the organic molecules were covalently attached to the silicon surface. The peaks between 1000 and 1100 cm^{-1} correspond to Si–OR stretching vibrations. The relatively low magnitude of these peaks indicates that oxidation of **2** was minimal. The hydrosilylation reaction of SiO_x containing **1** was unsuccessful, yielding unreacted SiO_x, which exhibited poor dispersibility.

The local environment of the silicon framework was examined using X-ray absorption near edge structure (XANES) analysis. The Si K-edge absorption spectra for **2** are compared with a (111) oriented p-type silicon wafer and amorphous SiO_2 in Figure 2b. The prominent peak at 1847 eV for SiO_2 arises primarily from Si 1s → O 2p transitions and is shifted by 7 eV to higher energy than that for the bulk Si edge due to the more positively charged Si in SiO_2. This peak serves as a sensitive fingerprint to identify and estimate the amount of SiO_2-like species present in the sample. The XANES from **2** exhibits features at an energy of 1844 eV, which is between those measured for both the Si and SiO_2 samples. After oxidation of **2** with water over a 10 day period, a new peak at 1847 eV was observed, which corresponds to SiO_2 and suggests the generation of a suboxide SiO_x species in the sheet framework (Figure S1). Thus, the peak at 1844 eV is assigned to the Si–C bond, which is the same bond energy as that for a tetra-coordinated silicon atom-bonded organic group.[8a]

Next, the oxidation state of Si in **2** was probed using X-ray photoelectron spectroscopy (XPS). The XPS spectrum displayed a Si 2p peak with a binding energy of 102.0 eV (Figure 2c), which suggests that only one site exists in the structure. The Si 2p spectra obtained from bulk Si (99.0 eV) and SiO_2 (104 eV) are very different from those of **2**, which is consistent with **2** not simply being a mixture of Si and SiO_2.

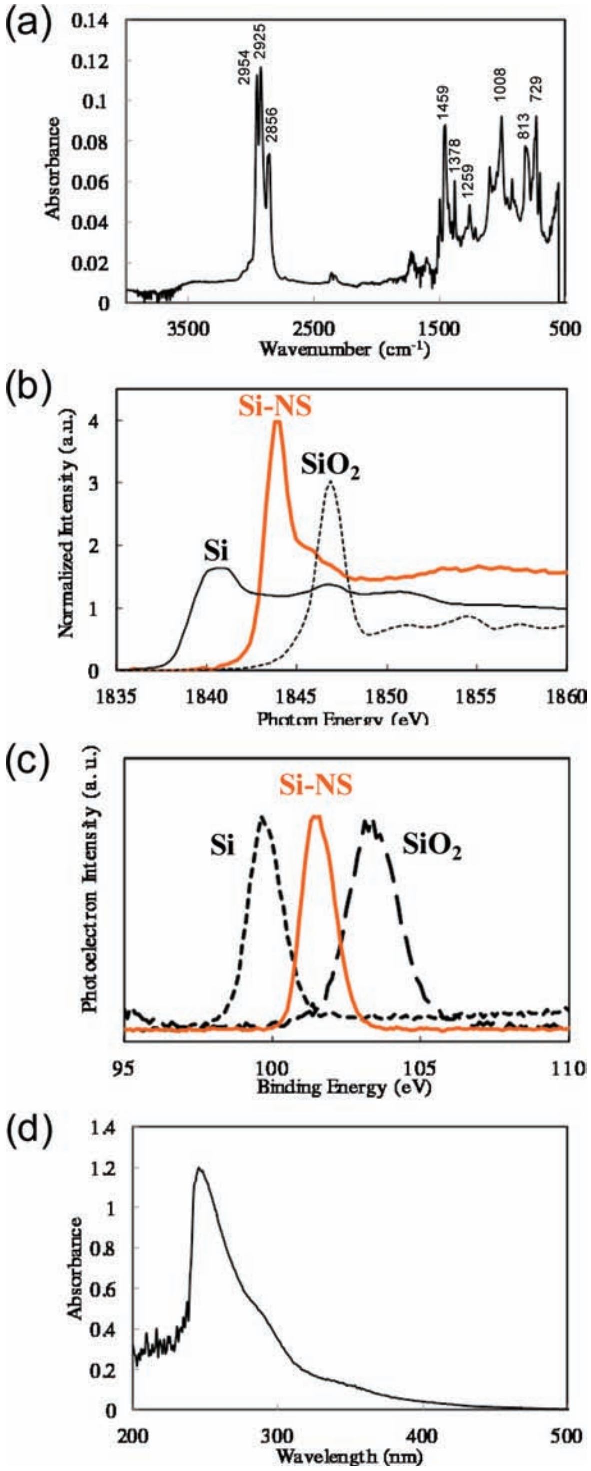

Figure 2. (a) FTIR spectra of **2**. (b) Si K-edge XANES spectra of **2** (brown line), Si(111) wafer and SiO_x (black line). The data was recorded at BL-10 in the Ritsumeikan SR Center. (c) XPS Si 2p spectra of **2** (brown line), Si(111) wafer and SiO_x (black line). (d) UV spectrum of **2**.

Recently, XPS data for decyl-capped silicon nanocrystals was reported, in which the peaks at 99 and 102 eV were attributed to the silicon core and surface Si-organo group and oxides, respectively.[16] No peak was observed at 99 eV in **2**, but the peak at 102 eV indicates that **2** does not have a core, but a bond attributed to a Si-organo group. This is evidence for the successful preparation of **2**.

The color of the hexane suspension of **2** was light-brown (Figure 1b), depending on the amount of Si, and exhibited optical properties that differed from those of **1**. There was a clear and substantial blue-shift of the absorption edge of **2** relative to **1**. More specifically, the absorption associated with the bandgap transition occurred at 4.2 eV for **2** (Figure 2d), which is in a shorter wavelength region than that for bulk silicon (1.1 eV)[17] and **1** (2.3 eV).[15] The bandgap is in good agreement with the theoretical direct bandgap for **1** (3 eV).[18] The absorption spectrum indicates the nature of the monolayer sheet, reflecting exfoliation into **2** in the organic solvent. Furthermore, this marked blue-shift can be understood by considering the changes in the density of the electron energy states due to the subnanometer thickness of **2**. Physicochemical investigation of semiconductor nanosheets is expected to become a fertile ground for research, and lead to novel applications of such two-dimensional silicon networks.

The atomic force microscopy (AFM) image of **2** dispersed in hexane and adsorbed on a highly oriented pyrolytic graphite (HOPG) substrate is shown in Figure 3. The thickness of the sheet was measured at intervals between the sheet and the substrate surface and gave a mean value of 3.1 nm. The structural model of **2** was constructed on the basis of the ideal formula $[Si_6H_3(C_6H_{13})_3]$. The model structure was optimized by minimizing the three-dimensional periodic lattice using force field mode in DISCOVER program. The thickness was calculated to be 2.3 nm on the basis of the atomic architecture (Figure 1d), indicating that **2** was composed of monolayer sheets.

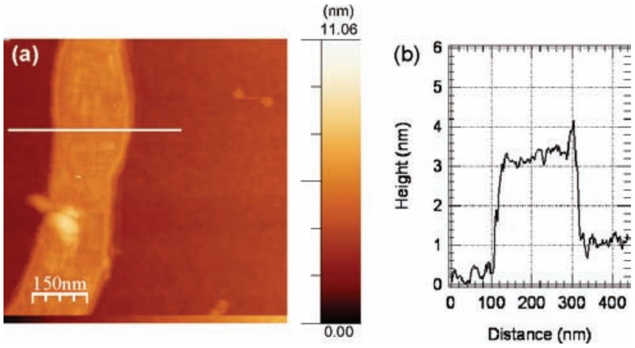

Figure 3. (a) Noncontact mode AFM image of **2**, and (b) its line profile taken along the white line in panel a.

Finally, the model structure of **2** is discussed. Figure 4a,b shows X-ray diffraction (XRD) patterns of **1** and **2**. The reflection peaks of **1** are broad and can be indexed on the basis of a hexagonal unit cell with a = 0.383 nm and c = 0.63 nm, which is consistent with previous data.[14] However, the reflection peak of drop-coated **2** on a glass substrate was a sharp peak at $2\theta = 12.4°$. The interlayer spacing is 0.71 nm, which is slightly larger than the original value of 0.63 nm for **1**. However, this expansion cannot be explained merely by the introduction on 1-decene (alkyl chain length of ca. 1.3 nm) into the interlayer space. Thus, the XRD data suggests that the peak at 12.4° is not the spacing of the expanding **1**, but indicates molecular-scale periodicity (0.71 nm) throughout **2**, which consist of silicon−hexane composites. Therefore, considering the FT-IR and XPS data, it was concluded that the layered structure of **1** has collapsed and changed to individual sheets by modification of the interlayer with hexane. The proposed structural model is presented in Figure 4c. The periodicity of hexyl groups on the sheet surface was estimated to be 0.71 nm, which strongly supports the observed structure being **2**, and confirms the periodicity of hexyl groups on the surface of the silicon sublattice.[8,9] This result provides further evidence that the two-dimensional silicon sublattice is maintained in **2**.

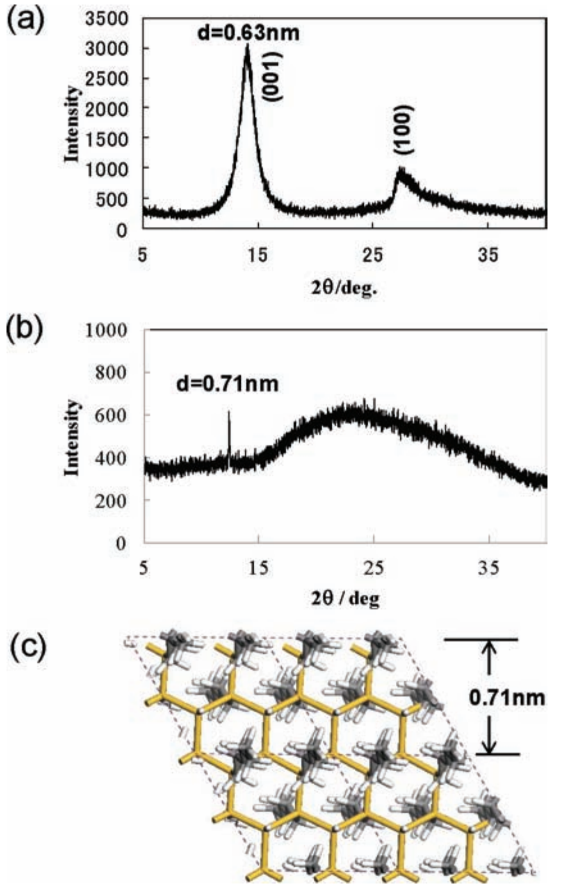

Figure 4. XRD patterns of (a) **1** and (b) **2**. (c) Top view of the atomic arrangement of **2** capped with hexane. The dashed line indicates the unit cell.

In summary, we have demonstrated a successful method for the synthesis of **2** incorporating different functional groups, and the resulting characteristics were investigated. This new silicon structure with the surface bonded to alkyl groups enables uniform dispersion in organic solvents. Therefore, polycrystalline silicon films for new types of sensors or other novel nanostructured devices could be prepared on any substrates by spin-coating of the sheet suspension at close to room temperature.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Preparation detail and XAFS data. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

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Notes

The authors declare no competing financial interest.

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