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Synthesis and Optical Properties of Monolayer Organosilicon Nanosheets

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The synthesis of silicon nanosheets for fabricating electronic devices without using conventional vacuum processes and vapor deposition is challenging and is anticipated to receive significant attention for a wide range of applications.[1] By using silicon nanosheets, a polycrystalline silicon monolayer coating can be formed on any object using a suspension containing the nanosheets, which can be organized in various ways through a soft-chemical procedure such as flocculation and self-assembly. However, there are no reports to date clearly demonstrating the synthesis and characterization of organosilicon nanosheets composed of a double-sided Si (111) surface.[2,3] Here, we report the synthesis of oxygen-free, phenyl-modified organosilicon nanosheets with atomic thickness. One consequence of this new silicon structure is its uniform dispersion in organic solvents, and the possibility of exfoliation into unilamellar nanosheets. The organosilicon nanosheets allow for the introduction of various organic groups on a silicon surface and could yield new silicon functional materials in diverse macrosystems.

We have previously attempted the fabrication of silicon nanosheets from the layered silicon compound $CaSi_2$. However, the surfaces of these nanosheets were found to be oxidized.[4] This was caused by the Si−H bond being unstable, leading to oxidation and hydrolysis. This is also one of the main reasons why silicon nanosheets easily aggregate and are difficult to disperse in a solvent, suggesting limitations for the choice of the fabrication method. The introduction of organic groups appears to be a useful method for the successful fabrication of silicon nanosheets without oxidation, because of their high dispersion in organic solvents and stability with respect to oxidation and/or hydrolysis, caused by the formation of a hydrophobic phase on the silicon surface.

First, to prepare oxygen-free organosilicon nanosheets, we carried out the synthesis of organosilicon nanosheets $[Si_6H_xPh_{6-x}]$ by the reaction of layered polysilane $[Si_6H_6]$[5] with phenyl magnesium bromide [PhMgBr]. Normally, an intermediate halogenation step is needed for the introduction of organic groups using the Grignard reagent on bulk Si (111) because of their low reactivity.[6] However, since modification of layered polysilane with the Grignard reagent succeeded without the halogen step, a higher reactivity of layered polysilane compared to bulk Si (111) is indicated. The material thus obtained is a colorless paste and is soluble in typical organic solvents such as hexane, chloroform, acetone, or ether, suggesting that the phenyl group successfully bonded to the silicon sublattice.

The IR spectrum of $[Si_6H_xPh_{6-x}]$ shows that vibrations of phenyl groups bonded to the silicon plane were observed at 1150 and 1410 cm^{-1} corresponding to the Si−Ph bond and at 1700−2000 cm^{-1} corresponding to the C═C bond of aromatics (see Figure S1 in Supporting Information). We also observed a peak at 2100 cm^{-1}, attributed to Si−H asymmetric vibration. The clear presence of characteristic vibrations of the phenyl group and hydrogen indicates that the organic molecules are covalently attached to the silicon surface.

^1H NMR spectroscopy of $[Si_6H_xPh_{6-x}]$ also supported the 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 (Figure S2). The extent of substitution on the silicon surface was determined to be approximately −H/−Ph = 2:1. From this result, we determined the composition of the organosilicon nanosheet to be $[Si_6H_4Ph_2]$.

The local environment of the silicon framework was examined by X-ray absorption near-edge structure (XANES) analysis. The Si K-edge absorption spectra for $[Si_6H_4Ph_2]$ were compared to the spectra for a HF-etched (111)-oriented p-type silicon wafer and amorphous SiO_2 (Figure S3). XANES from $[Si_6H_4Ph_2]$ exhibited features at energies of 1841 and 1844 eV. The lower peak at 1841 eV was at the same energy as that for the Si−Si bond in crystalline silicon terminated with hydrogen and layered polysilane.[7] The higher peak of 1844 eV was assigned to the Si−Ph bond, which is at the same energy as that for tetracoordinated silicon atom-bonded organic groups. In addition, no peaks corresponding to the Si−O bond were observed, even in measurements performed after storing the samples under air for 1 day (Figure S4). This peak serves as a sensitive fingerprint for identifying and estimating the amount of SiO_2-like species present in the sample. This sheet was found to be stable toward oxidation and hydrolysis even with terminating hydrogen atoms on the surface, and thus the material could be handled easily under air. Such increased stability of the material by the introduction of Si−C bonds is supported by previous reports on porous silicon[8] and silicon nanowires.[9]

An important point to be noted is that the organosilicon nanosheet was fabricated as monolayer sheets in an organic solvent. The photoluminescence spectrum of $[Si_6H_4Ph_2]$ in 1,4-dioxane was obtained using excitation at 350 nm (Figure S5). The emission shows a peak at 415 nm (3.0 eV), which is in a shorter region than bulk silicon (1.1 eV[10]) and $[Si_6H_6]$ (2.3 eV[11]). The position of the photoluminescence peak at 415 nm is in good agreement with the theoretical direct band gap for $[Si_6H_6]$ (3 eV[12]). The photoluminescence indicates the nature of the monolayer sheet, reflecting exfoliation into individual organosilicon nanosheets in an organic solvent. On the other hand, the emission by excitation at 350 nm for the $[Si_6H_4Ph_2]$ solid film shows four peaks at 415, 440, 465 (sh), and 505 nm (sh). It is suggested that there is an influence of the conformational and/or substituent effect for $[Si_6H_4Ph_2]$, showing similar properties as one-dimensional polysilane.[13]

Atomic force microscopy (AFM) and atomically resolved AFM revealed a periodic structure of the phenyl groups on the silicon surface. A contact mode AFM image of $[Si_6H_4Ph_2]$ dispersed in hexane adsorbed on an HOPG substrate is shown in Figure 1a.

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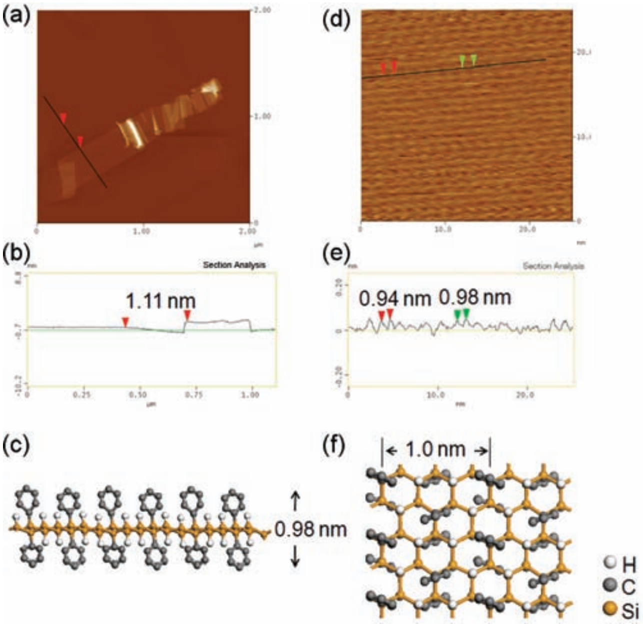

Figure 1. (a), AFM image of [$Si_6H_4Ph_2$] in contact mode. (b) Line profile along the black line in (a). (c) Side view of the model structure for [$Si_6H_4Ph_2$]. (d) Atomically resolved AFM image of the surface of [$Si_6H_4Ph_2$]. (e) Line profile along the black line in (d). (f) Top view of the model structure for [$Si_6H_4Ph_2$].

The thickness of the sheet was measured at intervals between the sheet and the substrate surface and yielded a mean value of 1.11 nm with a completely flat plane surface (Figure 1b). The structural model of the organosilicon nanosheet was constructed on the basis of the formula [$Si_6H_4Ph_2$]. The model structure was refined by minimizing the three-dimensional periodic lattice using the force field in the program DISCOVER. The thickness of the model structure for [$Si_6H_4Ph_2$] was calculated to be 0.98 nm on the basis of its atomic architecture (Figure 1c). The thickness and flatness of the surface were clearly demonstrated, indicating that the sample was composed of monolayer sheets. Interestingly, the sample had the shape of a band and showed a folded moiety. This indicates that the sample is very thin and flexible, similar to silk.

Atomically resolved AFM images of an individual sheet provided further insights into the structure of these nanosheets. An arrangement of atom-like dots on the top face was observed (Figure 1d). The closest distance between the dots was measured to be 0.96 ± 0.02 nm. In the [$Si_6H_4Ph_2$] structural model (Figure 1f), each phenyl group in the plane below is bonded to the silicon sublattice. The periodicity of phenyl groups on the model surface was estimated to be 1.0 nm, which is in good agreement with the closest distance between the dots in the AFM image. This strongly supports the observed structure being an organosilicon nanosheet, confirming the periodicity of the phenyl group on the surface of the silicon sublattice.

We carried out powder XRD measurements of the [$Si_6H_4Ph_2$] film to observe the periodic pattern of the phenyl group on the silicon surface, and we observed two broadened peaks (Figure S6). This broadening is due to aggregation of the organosilicon nanosheets, since broadened peaks for [$Si_6H_4Ph_2$] were observed at ca. $d = 1.0$ and 0.5 nm, which are in agreement with the periodicity of phenyl groups on the surface in our model.

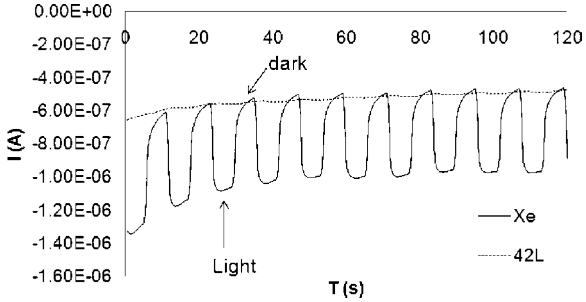

Figure 2. Light-induced photocurrent in the [$Si_6H_4Ph_2$] film. The solid line (Xe) indicates photocurrent in the sample with direct irradiation, and the dotted line (42 L) indicates photocurrent with irradiated light above 410 nm wavelength obtained using a filter.

Interestingly, light-induced photocurrent in the [$Si_6H_4Ph_2$] film was observed using a three-electrode photoelectrochemical cell (see the Experimental Procedure in the Supporting Information). The photocurrent was observed under direct irradiation of a xenon lamp, whereas it disappeared when the irradiation was cut off using a shutter. When a filter was used to cut off wavelengths less than 420 nm, no photocurrent was observed. The photocurrent thus showed a wavelength-dependence for the irradiation light, indicating that the photocurrent forms via a band gap transition. Considering that there is no previous report on photocurrent formation in polysilynes, the results in this study are very important.

We are currently applying this synthesis method for organosilicon nanosheets to incorporate different functional groups and investigate their characteristics. The development of the organosilicon nanosheet clearly has the potential for applications to new materials and methodologies, for example, a silicon wet process for solar cells.

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Supporting Information Available: Experimental procedure, Figures S1−10, and other informations of [$Si_6H_4Ph_2$]. This material is available free of charge via the Internet at http://pubs.acs.org.

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