

Synthesis of Siloxene Derivatives with Organic Groups

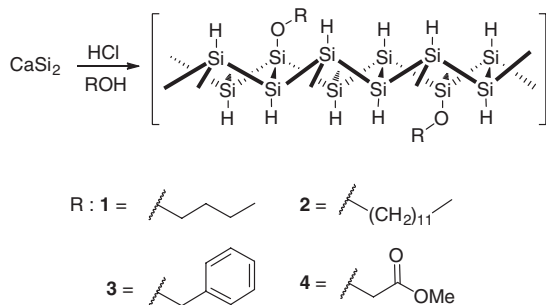
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Reaction of calcium disilicide (CaSi_2) and hydrogen chloride solution with various alcohols yields siloxene derivatives terminated with functional groups that are determined by the alcohol used as the solvent in the reaction. The functional groups terminated on silicon determine the basal spacing of the siloxene derivatives.

In the past decade, increased attention has been devoted to research on nanoscale materials, due to their extraordinary structures, electronic and optical properties, and potential applications in nanodevices.^{1,2} Siloxene is one such interesting material, because it consists of a two-dimensional silicon backbone and single silicon layers on a subnano scale.³ We have already reported the fabrication of monolayer siloxene by exfoliation from the Weiss siloxene $[\text{Si}_6\text{H}_3(\text{OH})_3]_n$, which afforded the possibility of application to layer-type nanocomposite systems using, for example, the layer-by-layer method.⁴ We have also investigated organic–silicon composite materials and reported the fabrication of a silicon nanosheet covered by organic groups.^{5,6} Organic moieties on a silicon nanosheet enable control of not only the basal spacing, but also the properties, for example, solubility in organic solvents and stability toward oxidation/hydrolysis. Therefore, the introduction of organic moieties to siloxene provides the possibility to control the structure and properties, which is important with respect to the development of siloxene as a building block for new silicon nanomaterials. In this work, we report on the synthesis and structure of organosiloxenes.

Weiss et al. reported the synthesis of organosiloxene with methyl and ethyl terminal groups.³ According to the reported method, the reaction of calcium disilicide (CaSi_2) with hydrogen chloride in an alcohol solution of was conducted in inert atmosphere to yield organosiloxenes **1–4**,⁷ that are insoluble in any organic solvent (Scheme 1). Infrared (IR) spectroscopy was used to identify and characterize the organic species on the silicon surface. When butanol was used as the solvent, the IR spectrum of the product siloxene **1** showed vibrations of Si–O



Scheme 1. The reaction of CaSi_2 with hydrogen chloride in alcohol.

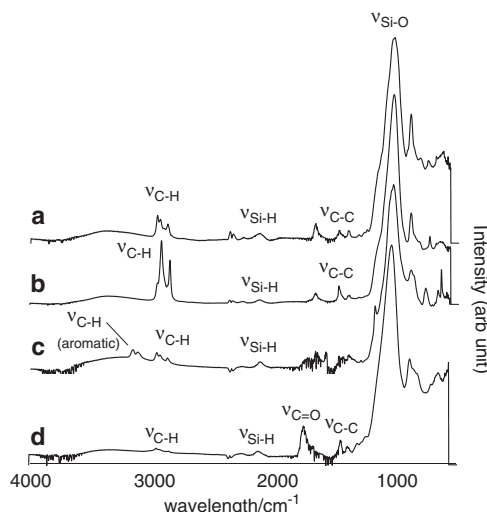


Figure 1. IR spectra of organosiloxene (a: **1**, b: **2**, c: **3**, and d: **4**).

(1010 cm^{-1}), C–C (1465 cm^{-1}), and C–H ($2850\text{--}2900\text{ cm}^{-1}$) (Figure 1a). A peak was also observed at 2100 cm^{-1} , which was attributed to a Si–H asymmetric vibration. The characteristic vibrations of the butyl group and Si–H bond indicate that organic molecules are covalently attached to the silicon surface through Si–O and Si–H bonds. The IR spectrum of **2** showed the same vibration pattern as that for **1**, and indicates the introduction of the dodecyl moiety on the siloxene (Figure 1b). The IR spectrum of siloxene **3**, prepared using benzyl alcohol as the solvent, showed the characteristic vibration for C–H bonds of an aromatic moiety at 3200 cm^{-1} (Figure 1c). For siloxene **4**, prepared using methyl glycolate, a C=O vibration was observed in the IR spectrum at 1743 cm^{-1} (Figure 1d). These examples confirm that organic substituents can be easily introduced to the siloxene using an alcohol that bears the desired organic moiety as the reaction solvent. It is considered that this method could also be applied to other organosiloxene systems.

The carbon contents in the organosiloxenes were determined by elemental analysis: 20.53 mass % for **1**, 35.40 mass % for **2**, 30.24 mass % for **3**, and 10.47 mass % for **4**. The formula for each of the organosiloxenes were assigned as approximately $[\text{Si}_6\text{H}_5(\text{OR})_n]$ (theoretical carbon content: 19.48% for **1**, 40.16% for **2**, 29.96% for **3**, and 13.72% for **4**, respectively). In the result of elemental analysis for compound **2** and **4**, the experimental carbon contents were less than theoretical value, which were caused from the partial oxidation during the preparation procedure. It is known that the Weiss siloxene $[\text{Si}_6\text{H}_3(\text{OH})_3]_n$ is terminated by three hydroxy groups in the six-membered silicon rings. However, these organosiloxene are mainly substituted by on alkoxy groups in the six-membered silicon rings, affording the formula of $[\text{Si}_6\text{H}_5(\text{OR})_n]$. The formula of $[\text{Si}_6\text{H}_5(\text{OR})_n]$.

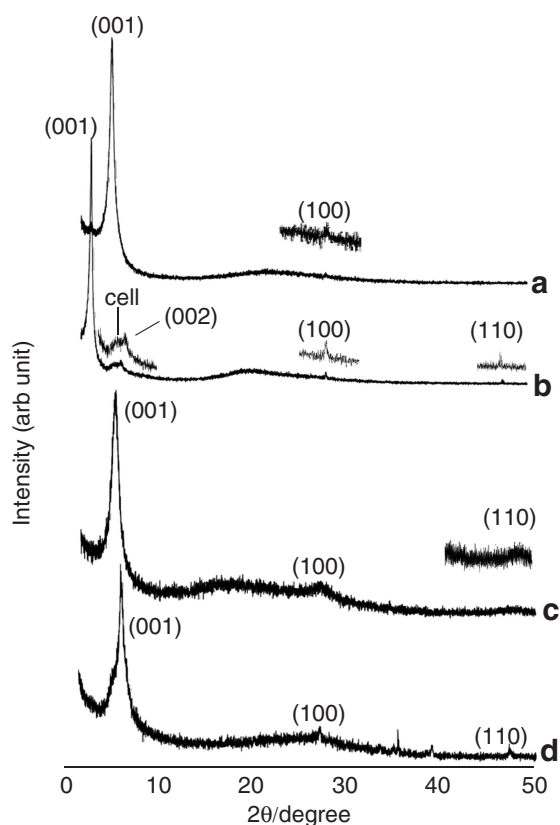


Figure 2. X-ray diffraction of organosiloxene (a: **1**, b: **2**, c: **3**, and d: **4**).

Table 1. Comparison of the basal spacing for organic siloxene

Compound	Hexagonal lattice constant a [Å]	Basal spacing $[d]$ [Å]	Increasing in basal spacing $\Delta [d]$ [Å]
Weiss siloxene: ³ $[\text{Si}_6\text{H}_3(\text{OH})_3]$	3.82	6.6	—
1 : $[\text{Si}_6\text{H}_5(\text{OBu})]$	3.84	16.7	10.1
2 : $[\text{Si}_6\text{H}_5(\text{OC}_{12}\text{H}_{25})]$	3.84	28.6	22.0
3 : $[\text{Si}_6\text{H}_5(\text{OBn})]$	3.83	15.6	9.0
4 : $[\text{Si}_6\text{H}_5(\text{OCH}_2\text{COOMe})]$	3.84	13.2	6.6

$\text{H}_5(\text{OR})_n$, which is less OR/H ratio than that of Weiss siloxene, is obtained due to the steric influence and rotation barrier of the more bulky substituent organic groups than the hydroxy group.

Figure 2 shows X-ray diffraction (XRD) patterns of siloxene **1–4**, with broad reflection peaks indexed on the basis of a hexagonal unit cell (Table 1). The basal spacing, or the lattice constant c , is comparable to that for siloxene as reported by Weiss et al.³ Each of the organosiloxenes **1–4** comprised a layered structure with wider basal spacing than the Weiss siloxene, and the increase in the basal spacing is dependent on the organic substituent introduced to siloxene. The basal spacing of compound **2** with dodecyl groups was much larger than the other modified siloxenes, which reflects the long chain length of the dodecyl groups. This result suggests that the basal space can be controlled by the selection of organic groups with the desired length. The silicon sublattice was confirmed from XRD

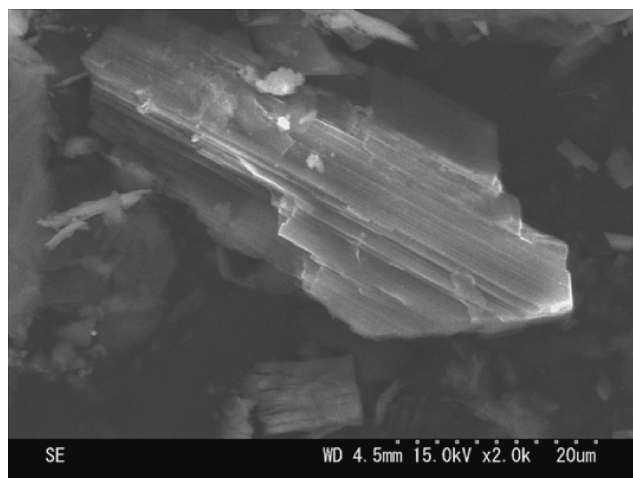


Figure 3. SEM image of organosiloxene **4**.

observations of broad (100) and (110) reflections with $a = 3.83\text{--}3.84$ Å, which correspond to a two-dimensional silicon framework composed of a double-sided Si(111) surface. The inplane hexagonal lattice constant coincides with that of CaSi_2 ($a = 3.85$ Å), which indicates that the reaction is topotactic and the two-dimensional silicon network of CaSi_2 is preserved.

Figure 3 shows a scanning electron microscope (SEM) image of siloxene **4** on carbon film with a structure in which thin layers of the organosiloxene are integrated. Thus, the organosiloxene crystals are composed of aggregations of thin sheets, which indicates the preparation of topochemically controlled products and is in agreement with the XRD results.

In summary, the reaction of CaSi_2 with hydrogen chloride in an alcohol solvent resulted in new organosiloxene derivatives, of which the structures were controlled by the organic groups introduced. We have developed these compounds and methods for functional organosilicon materials and investigated their optical and/or photoelectrochemical properties.

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References and Notes

- 1 A. Bachtold, P. Hadley, T. Nakanishi, C. Dekker, *Science* **2001**, *294*, 1317.
- 2 Y. Huang, X. F. Duan, Y. Cui, L. J. Lauhon, K.-H. Kim, C. M. Lieber, *Science* **2001**, *294*, 1313.
- 3 A. Weiss, G. Beil, H. Z. Meyer, *Z. Naturforsch., B* **1979**, *35*, 25.
- 4 H. Nakano, M. Ishii, H. Nakamura, *Chem. Commun.* **2005**, 2945.
- 5 H. Okamoto, Y. Kumai, Y. Sugiyama, T. Mitsuoka, K. Nakanishi, T. Ohta, H. Nozaki, S. Yamaguchi, S. Shirai, H. Nakano, *J. Am. Chem. Soc.* **2010**, *132*, 2710.
- 6 Y. Sugiyama, H. Okamoto, T. Mitsuoka, T. Morikawa, K. Nakanishi, T. Ohta, H. Nakano, *J. Am. Chem. Soc.* **2010**, *132*, 5946.
- 7 Supporting Information is available electronically on the CSJ-Journal Web site, <http://www.csj.jp/journals/chem-lett/index.html>.