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Similarities and differences of phonon modes in silicon materials depending on dimension: Raman spectroscopy of polysilanes and siloxene

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Abstract

We studied the –Si–Si– oscillations of all-trans-type polysilanes (poly(di-n-hexylsilane) and poly(di-n-butylsilane) at high pressure) and siloxene by Raman scattering spectroscopy. These are one- and two-dimensional silicon crystals. In these compounds, Raman peaks observed at less than 600 cm^{-1} corresponded to phonon modes at the Brillouin zone center and boundary of the three-dimensional silicon crystal (c-Si). In these polysilanes, the peaks corresponding to both optical and acoustic modes of c-Si have appeared, but in siloxene only the peaks corresponding to the optical phonon modes have been observed.

In recent years, low-dimensional silicon compounds, such as siloxene ($\text{Si}_6\text{O}_3\text{H}_6$) and polysilane ($-(\text{SiR}_1\text{R}_2)-$), have attracted interest. Polysilane has a one-dimensional silicon main chain. It has been reported that the backbone of poly(di-n-hexylsilane) (PDHS) has an all-trans structure (Fig. 1(a)) and that of poly(di-n-butylsilane) (PDBS) has a $7/3$ helical conformation. However, the conformation of PDBS at high pressure is all-trans [1]. Siloxene has a possibility of forming three different structures. One of them is the structure with Si planes terminated by H and OH (Si-planar type), which is considered to be a two-dimensional silicon crystal (Fig. 1(b)).

In single crystal silicon (c-Si), a Raman peak is found at 522 cm^{-1} , and in amorphous silicon (a-Si), peaks located at 475, 380, 310, and 150 cm^{-1} are observed [2]. In polysilanes, Raman peaks are found between 350 and 500 cm^{-1} [1, 3]. From a molecular point of view, several

different interpretations have been made concerning each of these peaks. In siloxene, peaks located at 380 and 515 cm^{-1} are assigned to oscillation modes of the Si plane, by calculation [4].

In this paper, we report the relation of Si oscillation modes among Si-containing compounds having different dimensions by Raman scattering spectroscopy. We re-examine oscillation modes of polysilanes from a crystal point of view, and the modes of above polysilanes and siloxene are compared to those of c-Si. The materials chosen for this comparative study were c-Si, PDHS, PDBS and Si-planar-type siloxene, because they contain the same structure, which is a zigzag structure of Si in this case.

The compounds PDHS and PDBS were synthesized by the reductive coupling of the corresponding dichlorosilane with metallic Na [5]. Si-planar-type siloxene was prepared by the reaction of CaSi_2 with aqueous hydrochloric acid at 0°C in a dark box [6]. The structure of this siloxene was identified by X-ray diffractometry [6].

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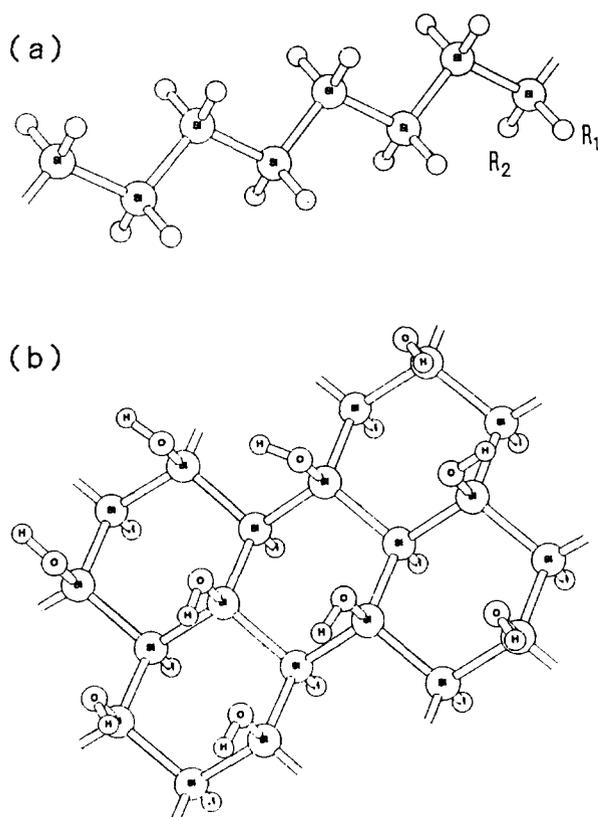


Fig. 1. The Si structure of (a) all-trans-type polysilane and (b) siloxene.

Raman spectra were obtained in a backscattering geometry by an NR-1800 Raman spectrometer (JASCO). The wavelength resolution was about 2 cm^{-1} . The pump beam was the 514.5 nm line of an Ar^+ laser. The high-pressure experiments were performed using a Merrill-Basset-type diamond anvil cell.

Fig. 2 shows the phonon dispersion of c-Si along the line from the Γ -point ($[0,0,0]2\pi/a$) to the K-point ($[\frac{3}{4}, \frac{3}{4}, 0]2\pi/a$) together with Raman spectra of PDHS, PDBS at high pressure and siloxene. The reason why we chose this line is that the main chain direction of an all-trans-type polysilane is a (110)-direction of c-Si, and a plane of Si-planar-type siloxene is formed by Si chain of (110)-direction. The Raman peaks less than 600 cm^{-1} almost coincide with the wave numbers of c-Si phonon bands at the Brillouin zone center and boundary and with the wave numbers of density of state peaks in c-Si. The peaks of PDHS (1 atm) and PDBS (2.6 GPa) at less than 300 cm^{-1} also agree with the above c-Si phonon bands. Existences of these peaks has been disregarded so far. In siloxene, peaks corresponding to c-Si acoustic

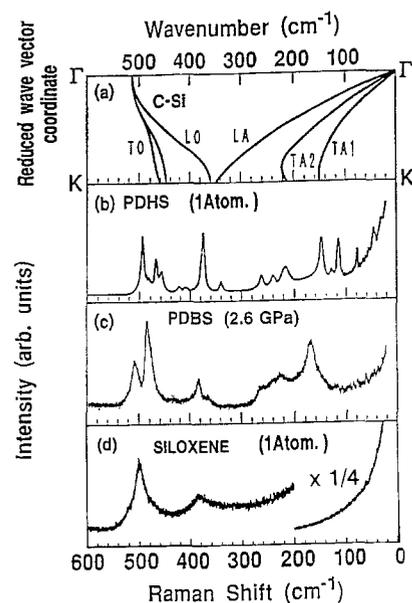


Fig. 2. Comparison between the dispersion relationship of three-dimensional silicon (a) and the Raman spectra of all-trans-type polysilanes, PDHS and PDBS, and Si-planar-type siloxene (b)–(d). The X-point of all-trans-type polysilanes compares with the K-point of the first Brillouin zone of a three-dimensional crystal silicon. This type of siloxene is formed by a $-\text{Si}-\text{Si}-$ chain oriented in K-direction of c-Si.

modes did not appear. We have made the same comparison between poly(di-n-hexylgermane) (PDHG) and a three-dimensional germanium crystal (c-Ge). The relationship of Raman spectra of PDHG and c-Ge is also the same as in the above silicon materials. The peak wave numbers in the Raman spectrum of all-trans-type PDHG [7] correspond to those of acoustic and optical phonon modes at Γ and K of c-Ge. This relationship implies that some oscillation modes and structure of unknown compounds composed of the IV group element can be assigned. All-trans-type polysilane and Si-planar-type siloxene should have phonon modes if the arrangement of silicon atoms in these compounds are periodic. The above considerations lead to the conclusion that Raman peaks less than 600 cm^{-1} in these Si materials can be attributed to phonons at the Brillouin zone center and boundary.

There are differences between the polysilanes and c-Si in the region corresponding to acoustic modes. In the cases of PDHS and PDBS, it is inferred that some peaks corresponding to c-Si TA1 and TA2 modes split into two or three peaks. We can expect this from the fact that the respective peak shapes are similar and that these peaks are shifted in the same way by applying pressure as

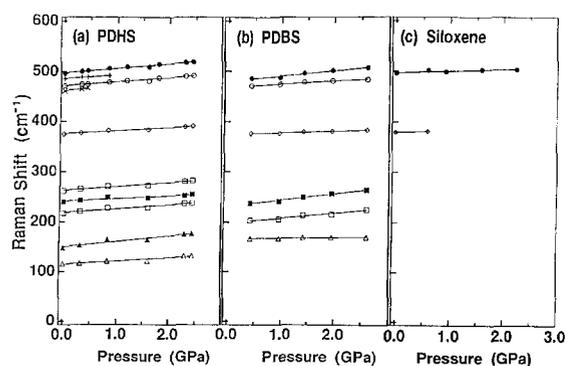


Fig. 3. Dependence of phonon mode frequencies of (a) PDHS, (b) PDBS, (c) siloxene on pressure. The solid lines show the least-squares fitting.

shown in Fig. 3. It is puzzling that the peaks corresponding to acoustic modes of one-dimensional Si split. The acoustic modes of siloxene did not appear.

The phonon vibrations of all-trans-type polysilane at the Brillouin zone center and boundary are represented by four atomic displacements. Ernst et al. have reported a vibrational study on anti-conformation of n-decamethyltetrasilane [8]. Their report and our study show that the vibrations of polysilanes agree with phonon modes of c-Si rather than with the four atomic molecular vibrations.

The agreement of phonon wave numbers among different dimensional compounds implies that the phonon interaction of these compounds between each point in the reciprocal lattice space is very small, i.e. anharmonic terms of the $-\text{Si}-\text{Si}-$ (and also $-\text{Ge}-\text{Ge}-$) oscillations are very small. Some of the phonon modes appear at points apart from those near the center of the Brillouin zone. It is reasonable to consider that the Si arrangement has some irregularities and this breaks the k -selection rule, which has already been observed in a-Si [2]. In a-Si, four modes appear in the frequencies close to those of the above polysilanes. This mixing differs from the X folding onto Γ found in Si/Ge superlattices. In these superlattices, no mixed peak is observed [9].

For acoustic modes, the shift wave numbers with increasing pressure of c-Si [10] and a-Si [11] at K are negative, but those of PDHS and PDBS

are positive (Fig. 3). Because the acoustic phonon at the zone boundary is related to bond bending [12], the bond bending of all-trans-type polysilane is different from that of c-Si and a-Si. For siloxene, the wave number shifts of the peaks corresponding to optical modes are similar to those of c-Si.

In summary, we have determined the assignment of $-\text{Si}-\text{Si}-$ oscillation modes of all-trans-type polysilanes (one-dimensional silicon crystals), and siloxene (two-dimensional silicon crystal). The oscillation modes correspond to the phonon modes of c-Si (three-dimensional crystal) at the Brillouin zone center and boundary. The acoustic modes of PDHS (1 atm) and PDBS (high pressure) appear, and some of them split. In siloxene, only peaks corresponding to optical modes are observed.

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