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## Structure and optical properties of ternary Si:C:H films prepared by evaporation of organo-polysilane

Shoji Furukawa†, Masahiro Obana†, Takeshi Nakamine†, Yuichi Shirakawa†, Ai Sorai† and Minoru Tamura†

† Department of Computer Science and Electronics, Kyushu Institute of Technology, 680-4 Kawazu, Izuka-shi, Fukuoka-ken 820, Japan

‡ Carbon and Inorganic Chemicals Planning Department, Mitsubishi Kasei Corporation, 2-5-2 Marunouchi, Chiyoda-ku, Tokyo 100, Japan

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**Abstract.** Ternary Si:C:H films are prepared by evaporating per-methyl-polysilane powder. The structure and optical properties of the films obtained are examined by various techniques. From infrared absorption and x-ray diffraction measurements, it is found that the film prepared at 27 °C contains a large number of Si backbones with an alternating *trans-gauche* conformation. The ultraviolet absorption spectrum shows a large peak at 300-350 nm and also supports the existence of one-dimensional Si chains. On the other hand, the film prepared at 300 °C contains a large number of helical backbones and shows a narrow absorption band at 300 nm. The strength of this absorption band strongly depends on measurement temperature, suggesting excitonic absorption.

### 1. Introduction

Silicon-based materials, such as hydrogenated amorphous silicon (a-Si:H), can be prepared by plasma chemical vapour deposition (Brodsky *et al* 1977), thermal chemical vapour deposition (Hirose *et al* 1977), and reactive sputtering (Lucovsky *et al* 1979). The growth rate of those methods is ordinarily of the order of  $1 \mu\text{m h}^{-1}$ , so various techniques have been developed in order to attain a high growth rate. For example, a growth rate higher by about one order of magnitude than that of the conventional methods has been achieved by plasma chemical vapour deposition using disilane gas (Furukawa and Matsumoto 1985), and by reactive sputtering using a planar magnet (Furukawa and Miyasato 1989).

In this paper, ternary Si:C:H films are prepared by evaporating per-methyl-polysilane powder, by which a growth rate of several micrometres per minute can be attained. The per-methyl-polysilane is stable even in air. However, there is not a good solvent for it. Therefore, the evaporation method is suitable for obtaining a film from the powder. The structure and optical properties of the films are examined by various measurements. As a result, it is found that the film prepared at 27 °C contains Si backbones with an alternating *trans-gauche* conformation. By changing the substrate temperature during evaporation, the Si backbone conformation can be controlled, and the corresponding change in the optical absorption spectrum is observed. These results are discussed in relation to the electronic structure obtained by the theoretical calculation.

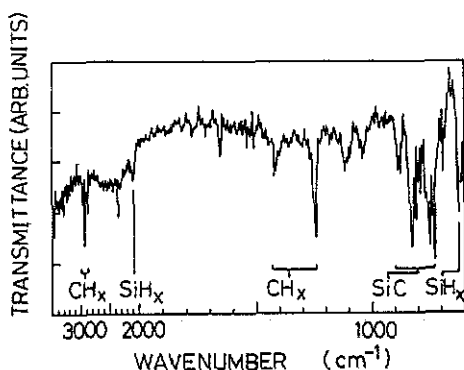


Figure 1. Infrared absorption spectrum for the film prepared at 27 °C.

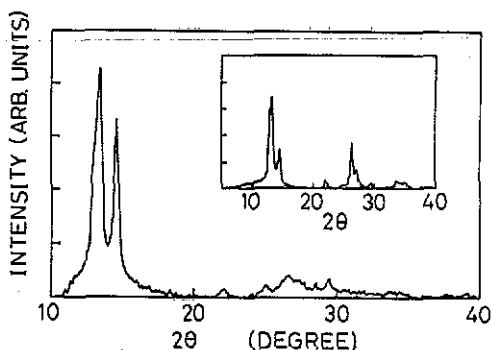


Figure 2. X-ray diffraction pattern for the film prepared at 27 °C ( $\theta$  is the diffraction angle). The inset shows the x-ray diffraction pattern for the per-methyl-polysilane powder.

## 2. Experiment

The materials used in this study were fabricated by evaporating the per-methyl-polysilanes  $[\text{Si}(\text{CH}_3)_2]_n$ ,  $n \simeq 2000$ , which was chemically synthesized. First, the per-methyl-polysilane powder and several substrates were placed in a boat-shaped holder on a molybdenum heater and a substrate holder, respectively, in a vacuum chamber. Then the chamber was evacuated to about  $10^{-6}$  Torr by a diffusion vacuum pump and a rotary vacuum pump. After evacuation, the material was evaporated by applying an AC of several tens of amperes. The distance between the substrates and the molybdenum heater was 10 cm, and the growth rate obtained was about several micrometres per minute. The material property was controlled by changing the substrate temperature from 27 to 300 °C during the deposition. The film (thickness of several micrometres) fabricated on a single-crystal Si wafer substrate was examined by infrared absorption (transmission type; 600–3500  $\text{cm}^{-1}$ ) and x-ray diffraction, and that on a quartz glass substrate was examined by optical absorption (200–900 nm).

## 3. Results and discussion

Figure 1 shows the infrared absorption spectrum for the film prepared at 27 °C. A single-crystal Si wafer was used as a reference for the measurement. It has been reported for the ternary Si:C:H material prepared by plasma chemical vapour deposition that absorptions occur at 630–650  $\text{cm}^{-1}$  (rocking mode of  $\text{SiH}_x$ ), 2000  $\text{cm}^{-1}$  (stretching mode of  $\text{SiH}_x$ ), 720–760  $\text{cm}^{-1}$  (stretching mode of SiC), 1377–1450  $\text{cm}^{-1}$  (deformation mode of  $\text{CH}_x$ ) and 2843–2936  $\text{cm}^{-1}$  (stretching mode of  $\text{CH}_x$ ) (Zanzucchi 1984). The corresponding absorption bands are observed (figure 1), so the film contains  $\text{SiH}_x$ , SiC and  $\text{CH}_x$  groups. (The absorption at 1250  $\text{cm}^{-1}$  is considered to be caused by the  $\text{CH}_x$  group.) In particular, the  $\text{CH}_2$  stretching absorption band in figure 1 clearly consists of a pair of peaks, which correspond to the asymmetric and symmetric modes. The increase in the  $\text{SiH}_x$  stretching absorption wavenumber by about 100  $\text{cm}^{-1}$  is probably caused by the increase in the effective electronegativity, arising from the formation of  $\text{SiH}_2$  or  $\text{CSiH}_x$  groups (Furukawa *et al* 1985).

Figure 2 shows the x-ray diffraction pattern ( $\theta$ - $2\theta$  scan) for the same specimen. The x-ray wavelength used was 0.154 nm (Cu  $K\alpha$  line). Apparent diffraction peaks are observed at  $2\theta = 14.14^\circ$  and  $15.64^\circ$ , which correspond to lattice spacings of 0.626 nm and 0.566 nm, respectively. The inset shows the similar diffraction pattern for the per-methyl-polysilane powder. In the inset, four diffraction peaks are observed at  $2\theta = 13.30^\circ$ ,  $14.57^\circ$ ,  $26.43^\circ$  and  $27.24^\circ$ , and they correspond to lattice spacings of 0.665 nm, 0.607 nm, 0.337 nm and 0.327 nm, respectively. From these values and the shapes of the diffraction peaks, it is considered that the latter two peaks are the higher-order reflections of the former two peaks. The difference between the diffraction angles of the film and the powder is considered to be caused by the difference in the Si-Si-Si angles of the Si backbone or by the experimental error arising from the roughness of the sample surface.

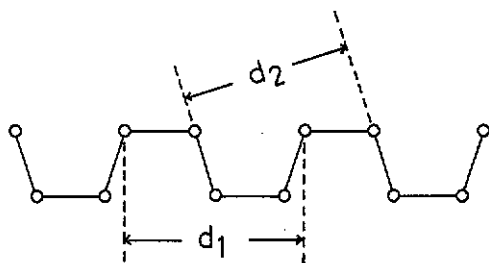


Figure 3. Configuration of the Si skeleton of the per-methyl-polysilane. In the figure, the side chains are not illustrated.

Figure 3 shows the most plausible configuration of the silicon skeleton in the film prepared at  $27^\circ$ . Theoretically, the distances  $d_1$  and  $d_2$  in figure 3 become 0.628 nm and 0.592 nm respectively, on the assumptions that the Si-Si-Si angle is a tetrahedral angle, and the distance between Si atoms is 0.235 nm. These values coincide with the lattice spacings deduced from the diffraction peaks in figure 2 within an error of 5%. Therefore, it is concluded that the film contains the one-dimensional Si backbones shown in figure 3, although it is obtained by the evaporation method. However, the chain length is reduced by the evaporation, because the second-order reflection is not observed. The result is consistent with the infrared absorption data, in which the absorption due to the  $\text{SiH}_x$  group is observed (see figure 1). Concerning the crystallographic symmetry of the present per-methyl-polysilane crystal, the details are not clear at the present stage, so other diffraction techniques should be performed in the future.

Although the infrared absorption spectrum shows the existence of various groups, such as  $\text{SiH}_x$ , SiC and  $\text{CH}_x$ , it is apparent from the x-ray diffraction pattern that three-dimensional Si networks are not formed in the film. The absence of the broad diffraction peak near  $2\theta = 30^\circ$  also excludes the existence of the amorphous Si network.

Figure 4 shows the optical absorption (200–450 nm) spectra for the film prepared at  $27^\circ\text{C}$ . (The measurement was performed in the range 200–900 nm. However, distinct absorption was not observed between 450 and 900 nm.) The full, broken and chain curves are for the data measured at  $-11^\circ\text{C}$ ,  $27^\circ\text{C}$  and  $80^\circ\text{C}$ , respectively. They do not show a monotonic change but do have a broad peak near 280–350 nm. This implies that the film contains plenty of one-dimensional Si chains. The temperature dependence of the spectrum indicates that the absorbance at the valley increases with increasing measurement temperature. The result can be explained by the increase in

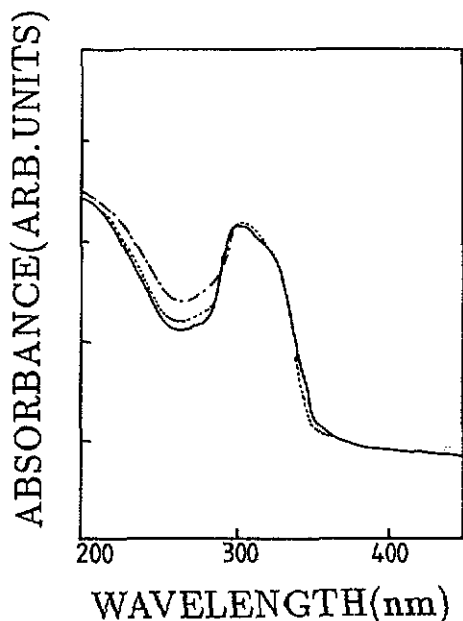


Figure 4. Optical absorption spectra obtained at various temperatures: —,  $-11^{\circ}\text{C}$ ; ---,  $27^{\circ}\text{C}$ ; - · -,  $80^{\circ}\text{C}$ .

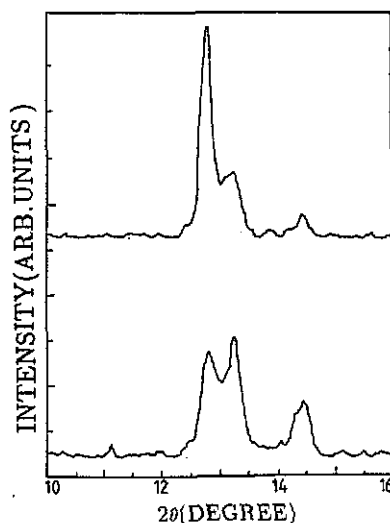


Figure 5. X-ray diffraction patterns for the films prepared at  $27^{\circ}\text{C}$  (lower) and at  $300^{\circ}\text{C}$  (upper). The former film was annealed at  $100^{\circ}\text{C}$  after the evaporation.

the proportion of disordered backbones (Moritomo *et al* 1991). The most important result obtained from figure 4 is that the absorption intensity at the peak hardly changes with change in the measurement temperature, suggesting an interband transition between the highest occupied valence band and the lowest unoccupied conduction band states in the one-dimensional Si chain (Takeda *et al* 1984).

Figure 5 shows the x-ray diffraction patterns for the film prepared at  $300^{\circ}\text{C}$  (upper pattern) as well as that for film prepared at  $27^{\circ}\text{C}$  (lower pattern). The latter specimen was annealed at  $100^{\circ}\text{C}$  for 1 h after the evaporation. In these spectra, three peaks are observed at  $2\theta = 12.82^{\circ}$ ,  $13.27^{\circ}$  and  $14.41^{\circ}$ , and the right-hand two peaks are considered to correspond to the peaks shown in figure 2. The lattice spacing corresponding to the lowest diffraction angle is 0.690 nm, and the slight increase in the spacing may arise from the change in the dihedral angle from the alternating *trans-gauche* conformation, i.e. a helical conformation. The likelihood of such a conformation increases with increasing preparation temperature, as shown in figure 5.

Figure 6 shows the optical absorption spectra for the film prepared at  $300^{\circ}\text{C}$ . The full, broken and chain curves are the spectra obtained at  $-11^{\circ}\text{C}$ ,  $27^{\circ}\text{C}$  and  $80^{\circ}\text{C}$ , respectively. A narrow absorption band is observed, and its peak height strongly depends on the measurement temperature. Therefore, it is suggested that the origin of the absorption is an excitonic excitation. This indicates that the absorption edge due to the interband transition is to the left of the 300 nm peak, i.e. at about 250 nm. This large shift in the absorption edge (due to the interband transition) from 300–350 nm (see figure 5) to 250 nm can be explained by the formation of the helical backbones (Mintmire 1989), and is consistent with the discussion concerning the x-ray

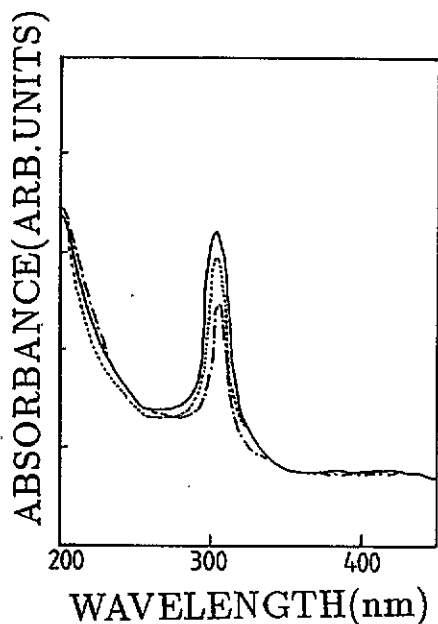


Figure 6. Optical absorption spectra obtained at various temperatures for the film prepared at 300 °C —, -11 °C ---, 27 °C - · -, 80 °C.

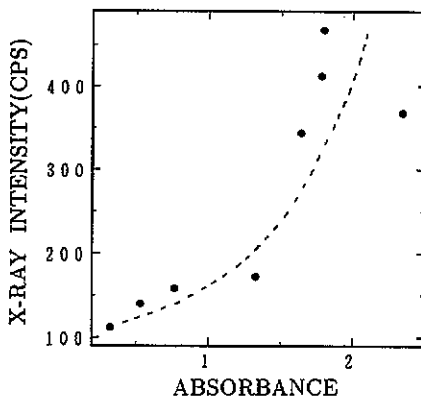


Figure 7. Relation between the x-ray diffraction intensity and the 300 nm absorption.

diffraction data.

From the Wannier exciton model, the energy difference between the conduction band minimum and the exciton level is inversely proportional to  $\epsilon^2$ , where  $\epsilon$  is the dielectric constant of the material. The dielectric constant of the present transparent film is smaller by several times than that of the conventional semiconductors. Therefore, the energy difference stated above becomes greater by about one order of magnitude than that of the conventional materials. This value (up to about 1 eV) is large enough for us to observe the excitonic absorption at 80 °C (thermal energy of about 0.03 eV).

Figure 7 shows the relation between the x-ray diffraction strength at  $2\theta = 12.82^\circ$  (the lowest diffraction angle) and the absorbance at 300 nm. It is apparent that the diffraction intensity positively correlates with the 300 nm absorption. These data clearly indicate that the origin of the 300 nm peak is not the disordered backbone but the ordered helical backbone.

#### 4. Summary and conclusion

In conclusion, ternary Si:C:H films have been prepared by evaporating the per-methylpolysilane powder  $[\text{Si}(\text{CH}_3)_2]_n$ ,  $n \approx 2000$ , and their structure and optical properties were examined via infrared absorption ( $600\text{--}3500\text{ cm}^{-1}$ ), x-ray diffraction, and visible and ultraviolet absorption ( $200\text{--}900\text{ nm}$ ). The x-ray diffraction pattern and the optical absorption spectrum show the existence of the one-dimensional Si chains. However, their length is reduced by the evaporation, which is confirmed from the appearance

of the infrared absorption band due to the  $\text{SiH}_x$  group as well as the reduction in the x-ray intensity of the second-order reflection. The Si backbone conformation can be controlled by changing the substrate temperature during the deposition. The film prepared at room temperature contains a large number of Si backbones having an alternating *trans-gauche* conformation, whereas the film prepared at 300°C contains helical Si backbones. The latter cause the widening of the energy gap, i.e. the difference between the energy levels of the highest occupied valence band and the lowest unoccupied conduction band states, and also cause excitonic excitation.

As stated above, ternary Si:C:H material having one-dimensional Si chains can be obtained by the present preparation method with a high growth rate, and its skeleton conformation can be controlled by changing only the substrate temperature during the deposition. Therefore, the method may be useful for fabricating new optical and electronic devices.

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