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Orientation of films prepared by the evaporation of poly(dimethyl silane)

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Abstract. This paper describes highly oriented films prepared by the evaporation of poly(dimethyl silane). The specimens are prepared at various evaporation speeds and substrate temperatures. The polymer is divided into species of about 2 nm length on the evaporation heater, and the species recrystallize on the substrate. The structure and orientation of the films are investigated using wide-angle x-ray diffraction and ultraviolet absorption methods. The substrates used are single-crystal silicon (100) for the x-ray diffraction measurement and fused silica for the ultraviolet absorption measurement. The polymer exhibits the same orientation on both substrates. It is found that most of the silicon chains are perpendicular to the substrate surface in the film prepared under the condition whose growth rate is lower than 20 nm min^{-1} . On increasing the substrate temperature, the number of silicon chains whose orientation is normal to the substrate surface increases.

1. Introduction

In recent years, polysilanes have been investigated with great interest, because of the characteristic properties arising from the one-dimensional silicon backbone. The polymers have been expected to be used for various applications, such as a one-dimensional electric conducting system [1–4], a generating source of third-harmonic light waves [5], and a high-resolution photoresist for electronic devices [6]. Polysilanes exhibit a characteristic ultraviolet absorption peak at 300–350 nm [6, 7]. The absorption depends strongly on the polarization of the incident light. Only when the electric field vector is parallel to the silicon backbone of the polymer, does the absorption spectrum exhibit a shaped strong peak. It has also been reported that the σ electron in the Si–Si chemical bond was delocalized around several silicon atoms [8]. The delocalized electron band structure was calculated [8], and the absorption peak was attributed to the $\sigma \rightarrow \sigma^*$ direct transition. However, the calculated band gap was larger than the energy obtained from the absorption peak. Therefore, a one-dimensional exciton model was also reported [9–11]. The electron was confined in the one-dimensional silicon-chain structure, and various phenomena were quite different from those of the three-dimensional bulk silicon crystal. In 1992, Kanemitsu *et al* [12] reported quantum size effects on the basis of the one-dimensional exciton model. The details are as follows: they synthesized polysilanes having different chain lengths and investigated the ultraviolet absorption spectrum of each specimen. Then, the absorption

peak energy was compared with the theoretical peak energy which was approximately and phenomenologically given by

$$E = E_{1D} + \left(\frac{\pi/(\pi - 2)}{N/2 + 2/(\pi - 2)} \right)^2 (E_{0D} - E_{1D}) \quad (1)$$

where E_{0D} and E_{1D} are the lowest excitation energies of disilane (6.2 eV) and the one-dimensional silicon backbone polymer (3.66 eV), respectively [13].

In order to observe these interesting characteristic features more definitely, and in order to apply polysilanes to the microdevices, control of the molecular orientation is very important. Recently, various multilayered polysilane films using the Langmuir-Blodgett (LB) technique were reported [14], and the orientation of films prepared under a high electric field between two close substrates was investigated. Furthermore, our group have reported an oriented poly(di-*n*-hexyl silane) film prepared by spreading a very thin heptan solution onto the Si(100) substrate [15]. However, these films were not easily applied to the microdevices, because the growth process of the films was not well controlled.

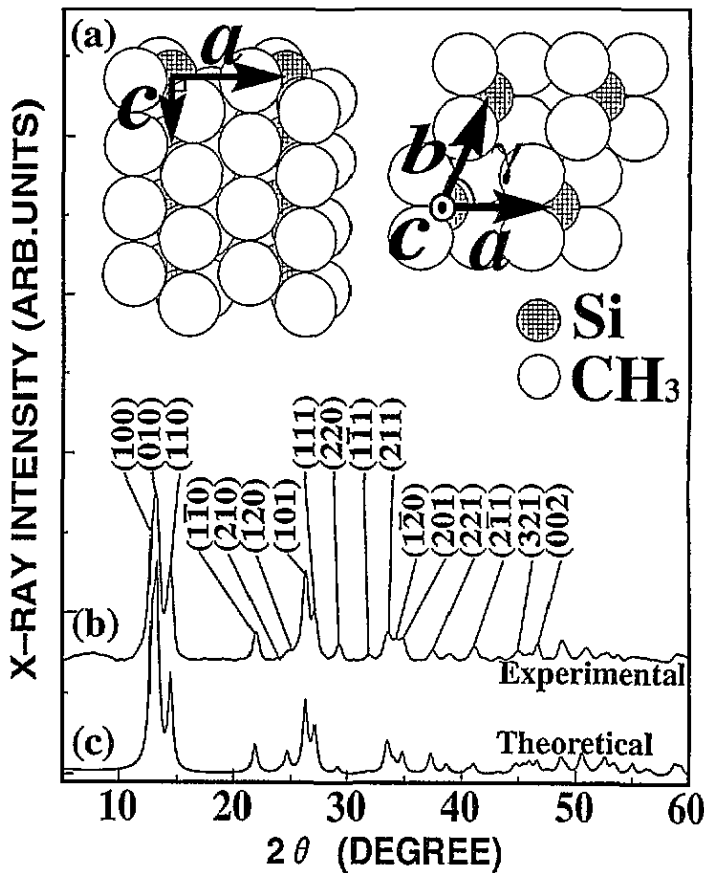


Figure 1. (a) Crystal structure of the poly(dimethyl silane) and (b) the experimental and (c) the theoretical x-ray diffraction patterns.

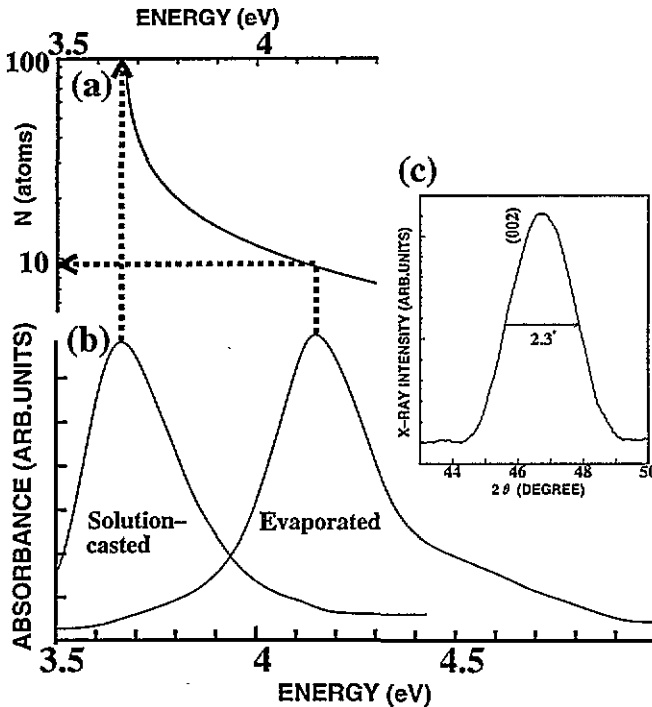


Figure 2. (a) Quantum size effect on the absorption peak energy, (b) ultraviolet absorption spectra of the evaporated and solution-cast films and (c) (002) x-ray diffraction pattern of the evaporated film.

In this work we have controlled the molecular orientation in the poly(dimethyl silane) evaporated film and obtained a highly oriented film in which most of the one-dimensional silicon backbones are perpendicular to the substrate surface. In order to investigate the molecular orientation, information on the crystal structure is very important. However, the crystal structure of the polysilanes has not been well studied. Fortunately, concerning the poly(dimethyl silane), we have determined the crystal structure and the inter-molecular structure in previous work [16]. The results are as follows: the crystals have a monoclinic unit cell with $a = 0.745$ nm, $b = 0.724$ nm, $c = 0.389$ nm and $\gamma = 67.1^\circ$, the primitive translation vector c is parallel to the silicon backbone, and each unit cell includes one polymer chain. The structure is different from the polyethylene's crystal structure. The conformation of the silicon backbone of poly(dimethyl silane) is all *trans*. Figure 1(a) shows the crystal structure of poly(dimethyl silane). The nearest polymer chains are reasonably packed to keep the van der Waals distance between the methyl substituents. Twin-like crystals attributed to the crystal structure of poly(dimethyl silane) have also been observed as the satellite peaks in the x-ray rocking curve. Figure 1(b) is the experimental x-ray diffraction pattern of the powdered material, and figure 1(c) is the calculated pattern using the obtained crystal structure. The theoretical pattern is in good agreement with the experimental pattern. Furthermore, the diffraction pattern for the powdered specimen prepared from the evaporated film has been observed, and the pattern is in agreement with figure 1(b). Therefore, poly(dimethyl silane) is recrystallized in the evaporated film as shown in figure 1(a).

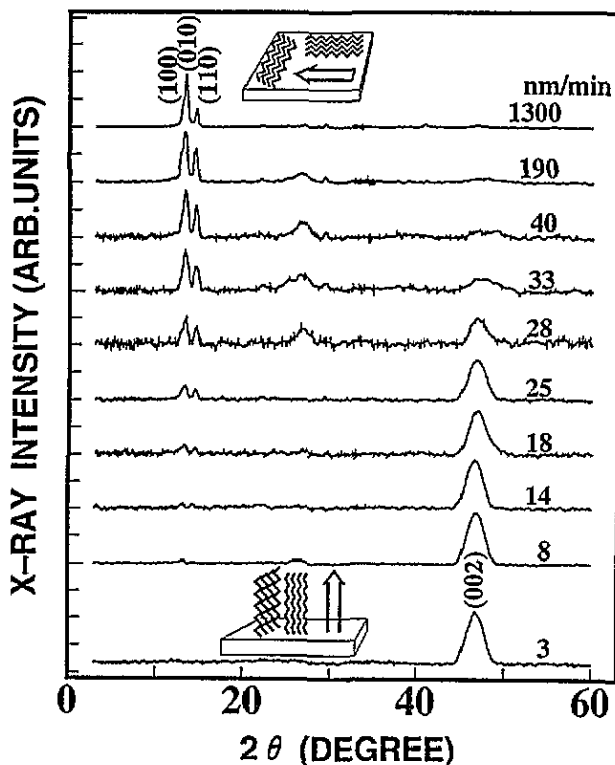


Figure 3. X-ray diffraction patterns of the evaporated films prepared at various evaporation speeds. The insets show the orientation of the film.

2. Experimental section

The poly(dimethyl silane) was chemically synthesized from dimethyldichlorosilane by means of the Waltz method. The thin polymer film was prepared using the vacuum evaporation technique. The powder of the specimen was put on the molybdenum boat-type heater, and the powder was heated by controlled AC. In order to investigate the optical properties, we used an ultraviolet absorption system with the transmittance mode. Concerning the x-ray diffraction measurement, the wavelength used was 0.154 nm (Cu $K\alpha$ line), and its power was 40 kV \times 80 mA.

3. Results and discussion

Figure 2(a) shows the quantum size effect of the lowest excitation energy of the one-dimensional silicon backbone materials calculated using equation (1). Figure 2(b) shows the ultraviolet absorption spectra of the evaporated and solution-cast thin films of poly(dimethyl silane). The absorption peak of the evaporated film is shifted towards higher energies compared with that of the solution-cast film. This blue shift of the absorption peak is explained by the size effect of the backbone. From figure 2(a), the chain length of poly(dimethyl silane) in the evaporated film is estimated to be about 2 nm, which corresponds to about ten silicon atoms of the one-dimensional backbone. Therefore, it

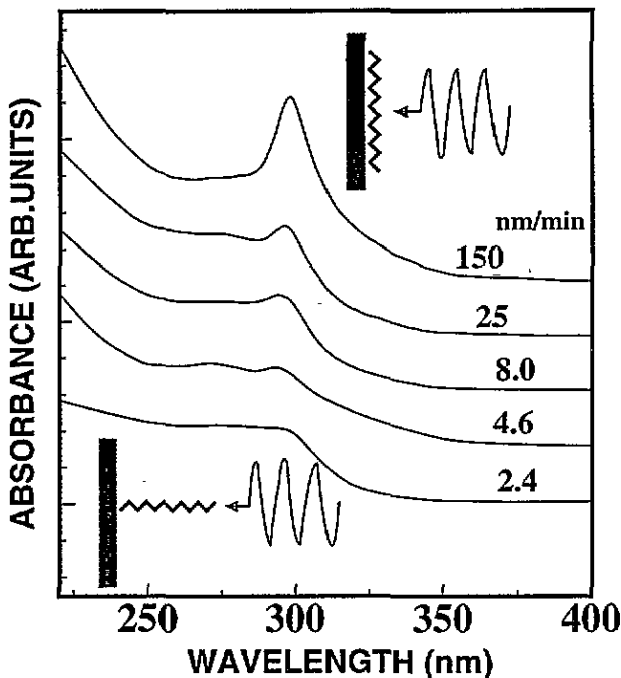


Figure 4. Ultraviolet absorption spectra of the evaporated films prepared at various evaporation speeds. The inset shows the molecular orientation and incident light.

is concluded that the chain length in the solution-cast film is not reduced from that of the chemically synthesized material, whereas it is reduced to $[\text{Si}(\text{CH}_3)_2]_n$, $n \simeq 10$, in the evaporated film. The chain length can also be roughly estimated from the half-width of the x-ray diffraction (002) peak shown in figure 2(c). The half-width is deduced to be 2.3° , indicating that the chain length is 1–2 nm. This is consistent with the result obtained from the ultraviolet absorption data. From these results, it is expected that the short chains of poly(dimethyl silane), which consist of about ten $\text{Si}(\text{CH}_3)_2$ groups, recrystallize on the substrate. This is similar to that of stearic acid having a constant chain length [17]. It is considered that the chain length is reduced by the thermal energy from the heater, and the species, whose molecular weights are reduced, are evaporated.

Figure 3 shows the x-ray diffraction patterns of the films obtained by varying the evaporation speed. Each pattern is normalized by the intensity of the (010) and (002) peaks. All the specimens were prepared at a substrate temperature of 13°C . The diffraction peaks indexed by (100), (010) and (110) appear only when the chains are parallel to the substrate surface, whereas the (002) peak appears when the chains are perpendicular to the substrate surface. The (001) peak does not appear theoretically for the all-*trans* confirmation.

The (010) peak as well as the (100) and (110) peaks appear for the films prepared at a high evaporation speed larger than 190 nm min^{-1} . Therefore, most of the chains are parallel to the substrate surface in those films. In that case, the rotation of the poly(dimethyl silane) crystal around the silicon backbone is considered to be arbitrary. For the films prepared at an intermediate evaporation speed of $28\text{--}40 \text{ nm min}^{-1}$, some of the chains are inclined from the surface normal direction, because the diffraction peaks appear at $20\text{--}30^\circ$. For the films prepared at a low evaporation speed, only the (002) peak appears in the diffraction

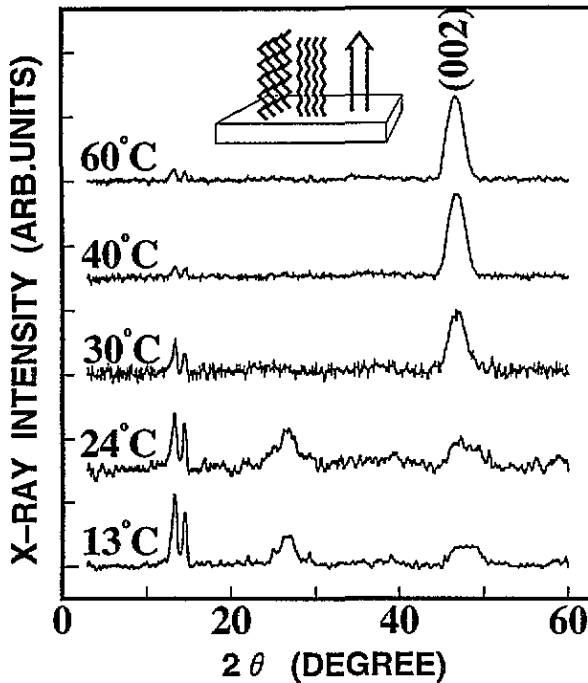


Figure 5. X-ray diffraction patterns of the evaporated films prepared at various substrate temperatures. The inset shows the orientation of the film.

pattern, indicating that the chains are perpendicular to the substrate surface.

The above results concerning the dependence of the molecular orientation on the evaporation speed can be discussed as follows: the evaporated species arrive at the growing surface with arbitrary rotation angle, and the concentration of the species is related to the evaporation speed. In the recrystallization process, the chains of the evaporated species (or molecules having a low molecular weight) move to their stable positions and rotate their silicon backbones to the equilibrium direction. When the evaporation speed is high, the species cannot move sufficient distance on the growing surface, because of the high concentration of the species. Therefore, the crystals exhibit three-dimensional growth rather than two-dimensional growth, causing the silicon backbones to become parallel to the substrate surface. On the other hand, when the evaporation speed is low, the species can move sufficient distance on the growing surface and rotate their silicon backbones to the equilibrium direction.

Furthermore, we have investigated the growth rate dependence on the ultraviolet absorption spectra, and the results are shown in figure 4. In the case of a high evaporation speed, the strength of the characteristic absorption peak concerning the one-dimensional silicon backbone, which appears at 300 nm, becomes strong. However, when the growth rate is low, the strength of the absorption peak becomes reduced. This result can be explained as follows: that is, when the growth rate is high, most of the silicon chains are parallel to the substrate surface, as shown in figure 3. In this case, the direction of the polarization vector of the incident light is parallel to the silicon backbone chains. On the other hand, when the growth rate is low, the chains are perpendicular to the substrate surface as well as the polarization vector of the incident light, which means that the incident light is not

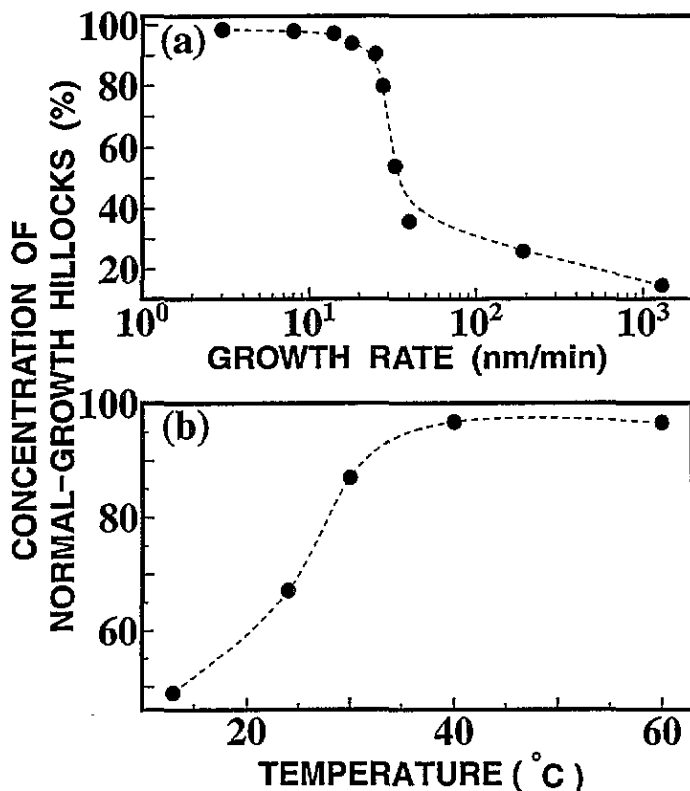


Figure 6. Orientation of the evaporated films as a function of (a) evaporation speed and (b) substrate temperature.

absorbed by the film. The result is consistent with the x-ray diffraction data. From these results, it is concluded that the short-chain poly(dimethyl silane) in the film prepared at a low growth rate becomes perpendicular to the substrate surface.

We have also investigated evaporated films prepared at various substrate temperatures. In the experiment, the evaporation speed was kept constant at 33 nm min^{-1} . Figure 5 shows the x-ray diffraction patterns of the films obtained. The diffraction pattern of the film prepared at 13°C does not show a particular orientation, whereas the pattern of the film prepared at a high substrate temperature shows a strong (002) diffraction peak. Therefore, the chains in the film prepared at a high substrate temperature are perpendicular to the substrate surface. It is considered that, when the substrate temperature is high, the species arriving at the growing surface can move sufficient distance to create two-dimensional crystals. This condition corresponds to the low evaporation speed discussed above.

Figure 6 shows a summary of the orientation of the evaporated films prepared under various conditions. These results were obtained by comparing the relative x-ray intensity of the (002) diffraction peak of the evaporated films with that of the powdered poly(dimethyl silane). The concentration of normal-growth crystals as a function of the growth rate is shown in figure 6(a). The step of the curve in figure 6(a) is explained by a reduction in the distance in which the evaporated species move freely as described earlier. Figure 6(b) shows the possibility of fabrication of a highly oriented film by controlling the substrate temperature during the deposition.

In conclusion, we have controlled the molecular orientation in the poly(dimethyl silane) evaporated film. The silicon backbones of poly(dimethyl silane) are perpendicular to the surface plane of the substrate when the film is prepared at a low evaporation speed and a high substrate temperature. When the evaporation speed is very high, the backbones are parallel to the substrate surface. The present work is expected to be applied to various microdevices and is expected to be used for further investigations of the one-dimensional silicon system.

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