

Structure and Orientation Control of Organopolysilane Thin Film Prepared by Vacuum Evaporation Technique

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Poly(di-methyl silane) $[\text{Si}(\text{CH}_3)_2]_n$ is the most fundamental polysilane. However, it is not solved in the organic solvent at room temperature. Therefore, the poly(di-methyl silane) thin film has been prepared by a vacuum evaporation method. In this paper, poly(di-methyl silane) thin films are prepared using new vacuum evaporation system, and the orientation of poly(di-methyl silane) chain has been examined as a function of vacuum pressure as well as substrate temperature during the evaporation. As a result, it is found that the orientation of poly(di-methyl silane) chain is strongly affected not only by the vacuum pressure but also by the substrate temperature during the deposition.

Key words: Poly(di-methyl silane), Organopolysilane, Vacuum Evaporation, Orientation, X-ray diffraction

1. INTRODUCTION

Organopolysilanes are expected to be used for future electronic and optical devices [1-4]. Electro-luminescent devices have been prepared using poly(di-methyl silane) and poly(methyl propyl silane) [5]. Poly(di-methyl silane) is the most fundamental polysilane. However, it is not solved in the organic solvent at room temperature. Therefore, the poly(di-methyl silane) thin film has been prepared by a vacuum evaporation method [5]. The orientation of poly(di-methyl silane) molecule can be controlled by changing evaporation speed as well as substrate temperature during the evaporation [6-8]. The direction of the chain of poly(di-methyl silane) molecule becomes perpendicular to the substrate surface when the evaporation speed is low and the substrate temperature is high. On the other hand, the direction of the chain becomes parallel to the substrate surface when the evaporation speed is high and the substrate temperature is low. Electric conductivity along the chain of poly(di-methyl silane) molecule is expected to be greater than that along the direction perpendicular to the chain. The optical properties are also expected to be controlled by changing molecular orientation.

As stated above, the molecular orientation can be controlled by changing evaporation speed and substrate temperature during the deposition. However, the substrate temperature and the evaporation pressure in the vacuum chamber may be changed by changing the current of the heater. Therefore, the substrate temperature and the pressure in the vacuum chamber should be well controlled during the evaporation.

In this paper, the substrate temperature, the temperature of the evaporator, and the pressure in the vacuum chamber are well controlled during the evaporation. And the effects of these parameters on the structure and the orientation of poly(di-methyl silane) are discussed on the bases of experimental data.

2. EXPERIMENTAL

The source powder material used in this study is $[\text{Si}(\text{CH}_3)_2]_n$, $n \sim 2000$ [7]. The source powder material was set on the Al_2O_3 crucible surrounded by spiral type tungsten heater in the vacuum chamber. The single-crystal (100) silicon wafer and the quartz glass substrates were also set in the vacuum chamber. The distance between the substrates and the heater was 34 [mm]. The chamber was evacuated by a rotary pump and a turbo molecular pump. The background pressure in the chamber was about 2×10^{-6} [Torr].

After the evacuation, the source powder material was evaporated onto the single-crystal silicon wafer and the quartz glass substrates. The specimen on the single-crystal silicon wafer substrate was then examined with a conventional X-ray diffractometer to obtain X-ray diffraction pattern as well as an optical absorption system to obtain infrared absorption spectrum. The specimen on the quartz glass substrate was examined with an optical absorption system to obtain ultra-violet and visible light absorption spectrum.

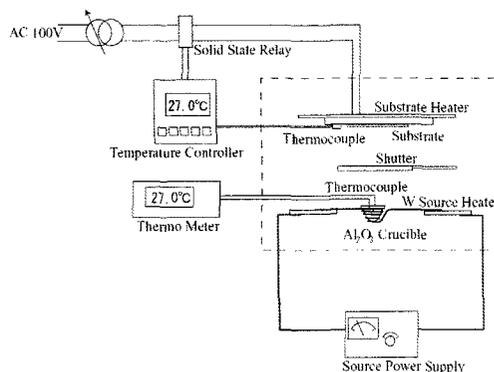


Fig.1 Schematic diagram of the vacuum-evaporation system used in this study.

In this study, the temperatures of the substrate and the heater were also measured during the evaporation. And

the X-ray diffraction pattern and the optical absorption spectra were measured as a function of temperatures of the substrate and the heater. Schematic diagram of the vacuum evaporation system used in this study is shown in Fig. 1.

3. RESULTS AND DISCUSSION

Figure 2 shows the previous results of the X-ray diffraction patterns as a function of evaporation speed [6]. The diffraction peaks appeared at $2\theta = 13\sim 15^\circ$ indicate (100), (010), and (110) reflections, and the peak appeared at $\sim 48^\circ$ indicate (002) reflection. Therefore, Fig. 2 shows that the poly(di-methyl silane) chain becomes parallel to the substrate surface when the evaporation speed is high, and the chain becomes perpendicular to the substrate surface when the evaporation speed is low [6].

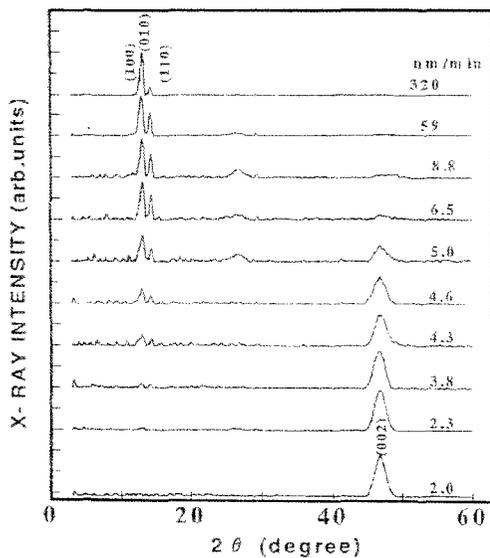


Fig.2 X-ray diffraction patterns as a function of evaporation speed.

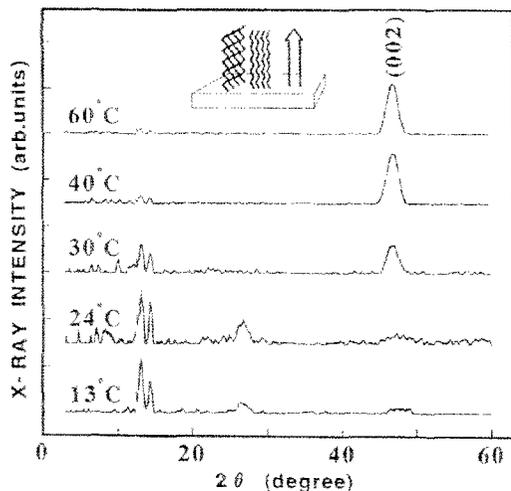


Fig.3 X-ray diffraction patterns as a function of substrate temperature during the evaporation.

Figure 3 also shows the previous results of the X-ray diffraction patterns as a function of substrate temperature during the evaporation. Figure 3 indicates that the poly(di-methyl silane) chain becomes parallel to the substrate surface when the substrate temperature is low, and the chain becomes perpendicular to the substrate surface when the substrate temperature is high [6].

Figure 4 shows the present results of the X-ray diffraction patterns as a function of substrate temperature during the evaporation. In this paper, the substrate temperature was changed from 303 K to 453 K. The temperature of the heater was held constant at 573 K. As shown in Fig. 4, the strength of the diffraction peaks appeared at $2\theta = 13 \sim 15^\circ$ as well as $\sim 48^\circ$ is changed with a change in substrate temperature during the evaporation. The three diffraction peaks appeared at $2\theta = 13 \sim 15^\circ$ correspond to (100), (010), and (110) reflections of the monoclinic unit cell of poly(di-methyl silane) crystal. All these three peaks appear when the poly(di-methyl silane) chains are parallel to the substrate surface. However, the molecular orientation at the interface between the poly(di-methyl silane) film and the substrate is changed with a change in diffraction strength of the (100), (010), and (110) reflections.

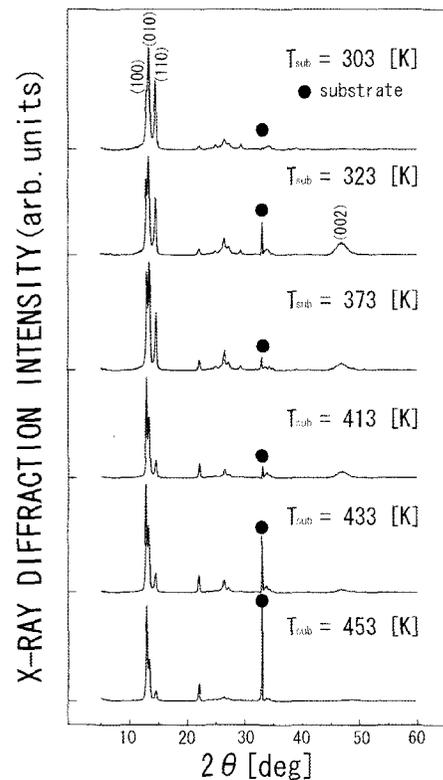


Fig.4 X-ray diffraction patterns as a function of substrate temperature during the evaporation.

These circumstances are shown in Fig. 5. The molecular orientations in Figs. 5 (a), (b), and (c) correspond to (100), (010), and (110) reflections, respectively. *a*, *b*, and *c* denote the primitive translation vectors of the monoclinic unit cell (sub-cell) of poly(di-methyl silane) crystal. In all of these three figures, the primitive translation vector *c* is parallel to

the substrate surface. However, the molecular orientation at the interface between the poly(di-methyl silane) film and the substrate is changed with a change in diffraction strength of the (100), (010), and (110) reflections.

Figure 6 shows the ratios of the X-ray diffraction

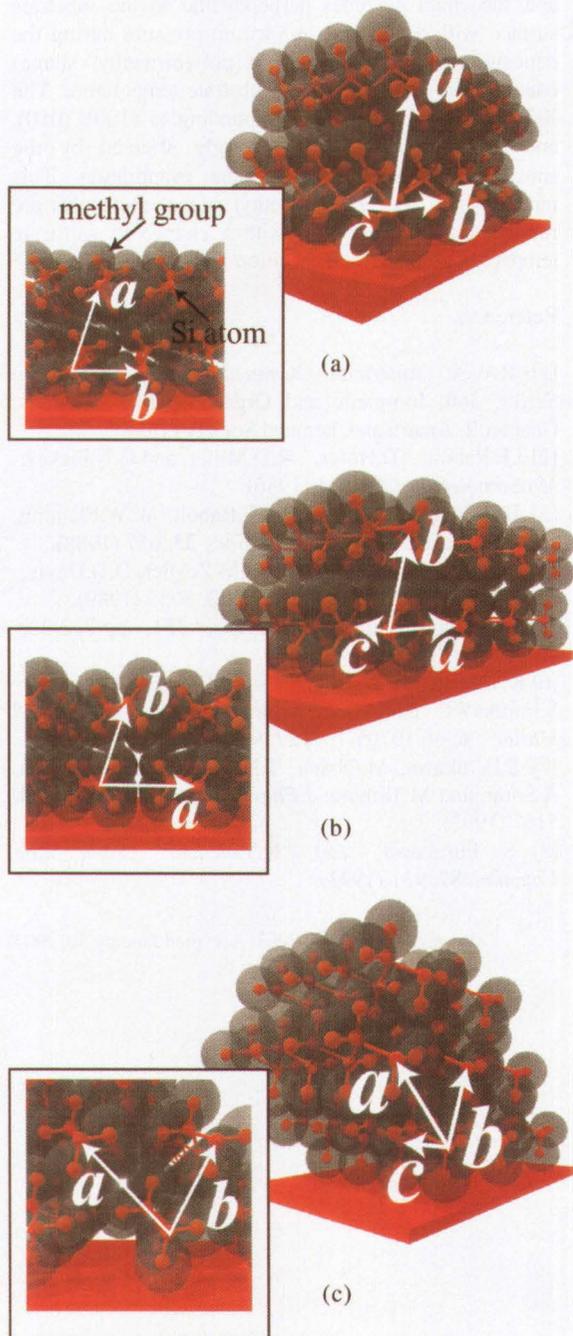


Fig.5 Relation between the molecular orientation and the (100), (010), and (110) reflections. *a*, *b*, and *c* denote the primitive translation vectors of the monoclinic unit cell of poly(di-methyl silane) crystal.

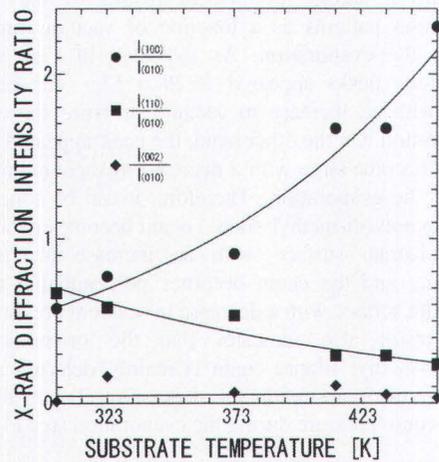


Fig.6 Ratios of X-ray diffraction peaks between $2\theta = 13\sim 15^\circ$ and $\sim 48^\circ$.

peaks appeared between $2\theta = 13 \sim 15^\circ$ and $\sim 48^\circ$. The ratio of the (100) peak to (010) peak is increased with an increase in substrate temperature during the deposition. On the other hand, the ratio of the (110) peak to (010) peak is decreased with an increase in substrate temperature during the evaporation. The ratio of the (002) peak to (010) peak is almost constant.

Figure 7 shows the present results of the optical absorption spectra as a function of substrate temperature during the evaporation. The optical absorption peak appeared at ~ 300 nm is come from Si-Si bond of the chain of poly(di-methyl silane).

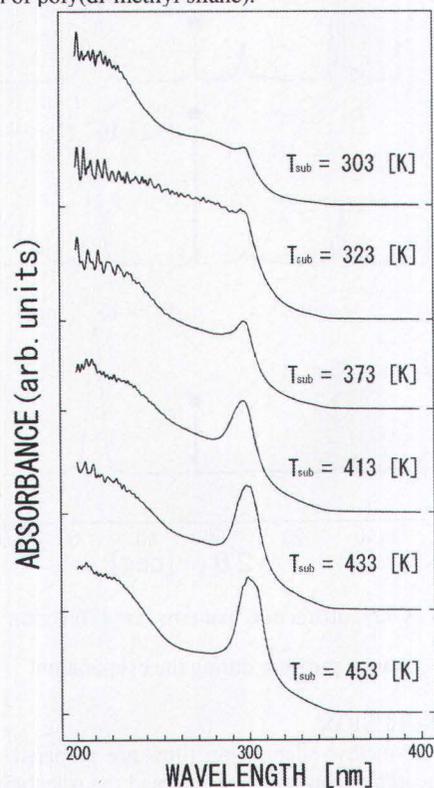


Fig.7 UV-VIS absorption spectra as a function of substrate temperature during the evaporation.

Figure 8 shows the present results of the X-ray diffraction patterns as a function of vacuum pressure during the evaporation. As indicated in Fig. 8, the diffraction peaks appeared at $2\theta = 13 \sim 15^\circ$ become large with an increase in vacuum pressure during the evaporation. On the other hand, the peak appeared at $2\theta \sim 48^\circ$ become large with a decrease in vacuum pressure during the evaporation. Therefore, it can be concluded that the poly(di-methyl silane) chain becomes parallel to the substrate surface with an increase in vacuum pressure, and the chain becomes perpendicular to the substrate surface with a decrease in vacuum pressure [8]. This result also indicates that the orientation of poly(di-methyl silane) chain is mainly determined not only by the evaporation speed (see Fig. 2) but also by the vacuum pressure during the evaporation (see Fig.8).

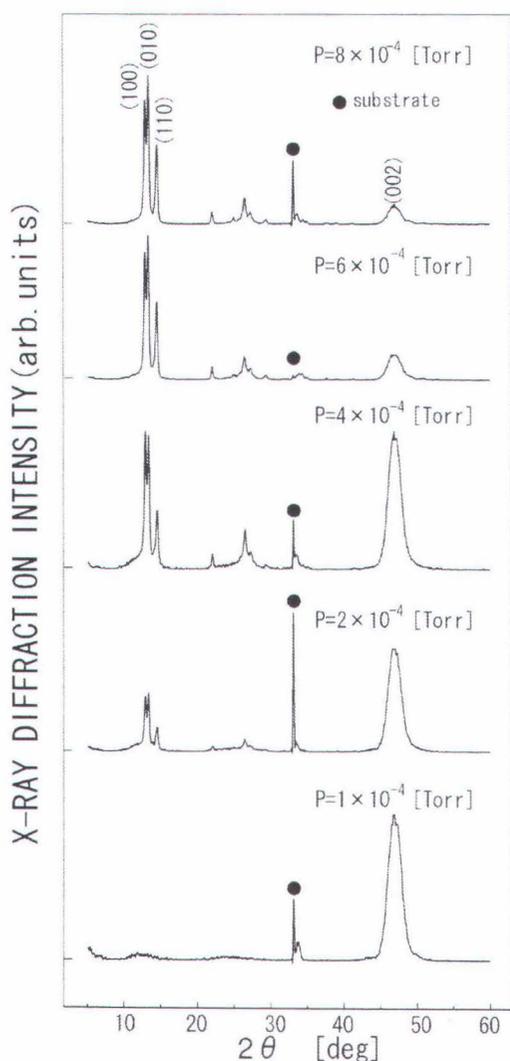


Fig.8 X-ray diffraction patterns as a function of vacuum pressure during the evaporation.

4. CONCLUSION

Poly(di-methyl silane) thin films are prepared using new vacuum evaporation system, and the orientation of poly(di-methyl silane) chain has been examined as a function of vacuum pressure as well as substrate

temperature during the evaporation. As a result, it is found that the orientation of poly(di-methyl silane) chain is strongly affected not only by the vacuum pressure but also by the substrate temperature during the evaporation. The poly(di-methyl silane) chain becomes parallel to the substrate surface with an increase in vacuum pressure, and the chain becomes perpendicular to the substrate surface with a decrease in vacuum pressure during the deposition. The orientation of poly(di-methyl silane) chain is also affected by the substrate temperature. The X-ray diffraction peaks corresponding to (100), (010), and (110) reflections are strongly affected by the substrate temperature during the evaporation. This indicates that the poly(di-methyl silane) molecules are rotated around the *c* axis with a change in substrate temperature during the deposition.

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