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A study on liquid-to-solid silicon conversion

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1. Introduction

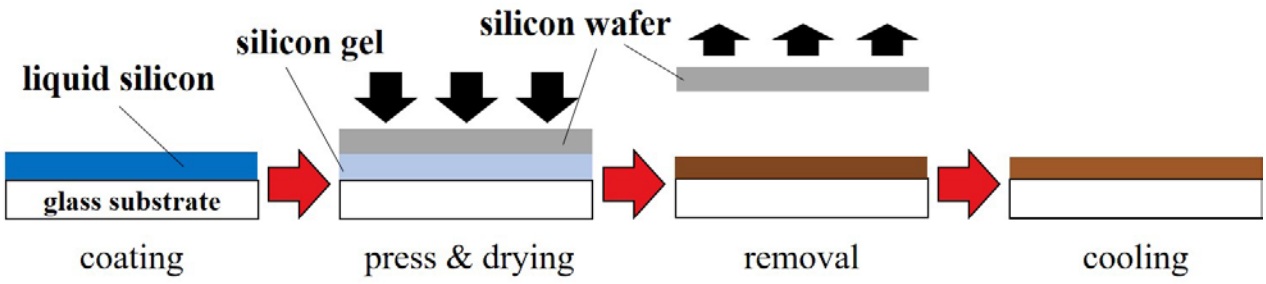
Liquid silicon, which was synthesized by Shimoda laboratory, is a precursor solution for semiconducting silicon. This material is a polydihydrosilane (polysilane; $-(SiH_2)_n-$) solution diluted with organic solvent, in which polysilane was obtained from cyclopentasilane(CPS) by photo-induced polymerization[1] [2]. The coated polysilane was converts to a semiconducting silicon by thermal dehydrogenation. The liquid-to-solid conversion passes through a gel state which has good deformability and molding properties in nanoimprinting processes. This feature is expected to be an alternative method to photolithography in microfabrication technique of semiconducting silicon.

Obviously, viscoelastic properties of the silicon gel is important for nanoimprinting process. However, the systematic study of the gel has not been investigate yet, except for a brief discussion of a Fourier Transform Infrared Spectroscopy (FTIR) measurement related to gel structure in a work by Masuda et al. They mentioned that the unhomogeneous gel phase might be appeared in polysilane film during the liquid-to-solid conversion. The purpose of this research is to observe the inhomogeneous phase that appeared in the gel film. Moreover, we associate the characteristics of the gel with imprinting properties to improve the imprinting properties.

2. Experimental

2-1. Pressure induced phase separation

Phase separation was induced in polysilane film by pressing a flat silicon wafer as a mold, as shown in Fig. 1. Liquid silicon was coated on a glass substrate and was dried at 100-220°C to obtain gel films. Then the film was pressed by the flat silicon mold at 1 MPa for 5 min while maintaining the drying temperature. The resultant films were observed by optical microscope



Olympus BX-51.

Fig. 1. Experimental procedure of pressure induced phase separation

2-2. Etching of Silicon gel

Here, inhomogeneous phase in the gel film was emphasized by dissolving a part of the film, as shown in Fig. 2. The gel film was obtained according to aforementioned processes at 100, 150, 180, and 220°C. The resultant films were dipped in etchant solution for 10 min, in which SUN-X (WAKO chemical) etching solution diluted by 1000 times with pure water was used. Since a part of the film was dissolved, the surface of the film was measured by Scanning Electron Microscope (SEM). The experimental was conducted in a glove box with a nitrogen atmosphere except when dipping process.

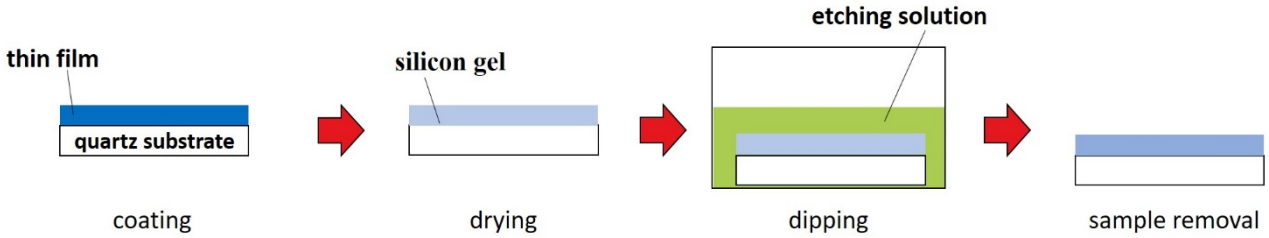


Fig. 2. Experimental procedure of etching of Silicon gel

3. Results and discussion

3-1. Pressure-induced phase separation

Fig. 3 shows optical microscope image of the sample that obtained in accordance with the procedure in section 2.1. Although chemical composition in the gel is homogeneous (only two element; silicon and hydrogen), the resultant patterns were inhomogeneous. Obviously, spinodal decomposition patterns were appeared in the films, indicating the fact that inhomogeneous phases exist in the gel film and it was emphasized by pressure, as pressure-induced phase separation. Fluctuation mode based on inhomogeneous phase grew in spinodal decomposition under applying pressure. No spinodal decomposition patterns were observed in an area that was under non-pressure.

The patterns what was separated will be discussed in next section.

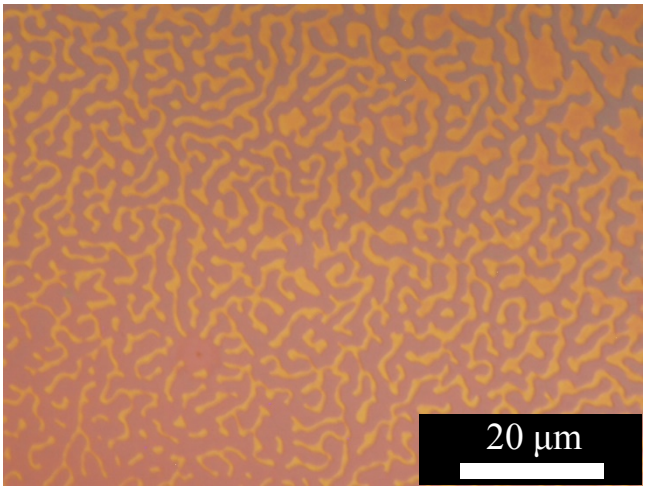


Fig. 3. Spinodal decomposition patterns (The sample of dried at 150℃, pressed at 1MPa)

3-2. Etching of silicon gel

Fig. 4 shows SEM images of gel films that obtained in accordance with the procedure in section 2.2. Fig. 4(a), which is the images before wet etching, shows uniform surface for all samples. After wet etching, a part of the gel was dissolved, and network-like structure was remained as shown in Fig. 4(b). The network structure appeared at 100°C, and it grew with drying temperature from 100°C to 150°C followed by it developed most at 180°C. When the drying temperature was at 220°C, the structure was developed excessively, and no longer network, but porous film. Silicon gel consisted of two phase that has different solubility, and composition ratio of the two phase was depended on drying temperature.

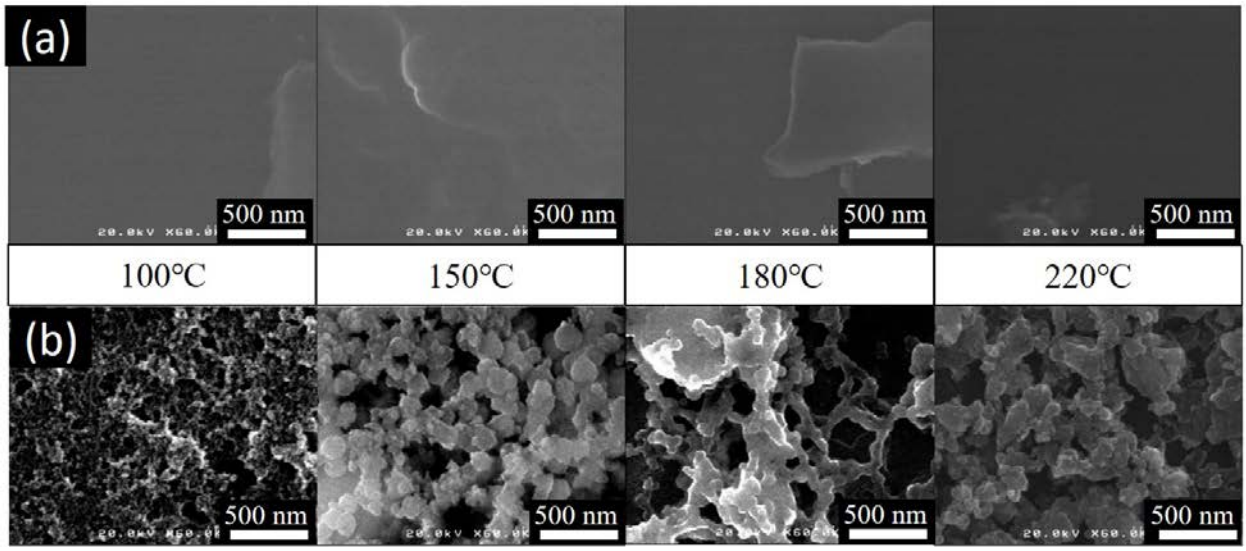


Fig. 4 Top view SEM images of gel films with drying temperature at 100, 150, 180, and 220°C. Each films were obtained in accordance with the procedure in section 2.2. (a) Before wet-etching and (b) after wet-etching.

Gel films with difference drying temperature were investigated by FTIR measurement. Fig. 5(a) shows the spectra in the wavenumber range of 2000 to 2300 cm^{-1} for the gel films dried at 20°C to 260°C[4]. The peaks appeared at 2150 cm^{-1} were divided into three peaks at 2135 cm^{-1} (red), 2105 cm^{-1} (blue), 2080 cm^{-1} (green) as SiH_3, SiH_2, and SiH stretching modes, respectively. Dehydrogenation was induced by heating, as shown in Fig. 5(b) in which integrated intensity of each peaks for the film with different drying temperature were plotted.

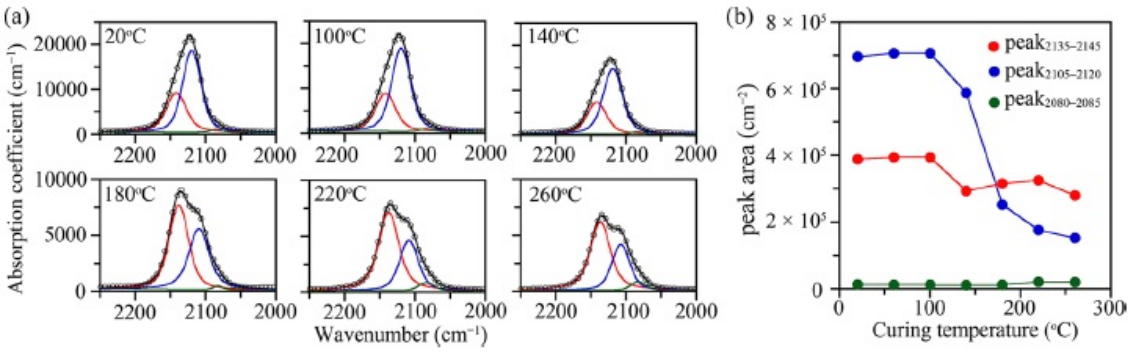


Fig. 5 FT-IR spectra for the films prepared at 20-260℃. (a) absorption spectra of Si-H stretching motion appearing at 2000–2300 cm^{-1} (b) plotted the prepared temperature dependence of each peaks area[4]

This dehydrogenation process was reported as in Fig. 6[4]. Since bonding energy of Si-H bond is weaker than that of Si-Si bond, the hydrogen atoms are released followed by the generated silicon radical bonds as Si-Si to construct silicon network structure. Therefore, silicon network develops with dehydrogenation process.

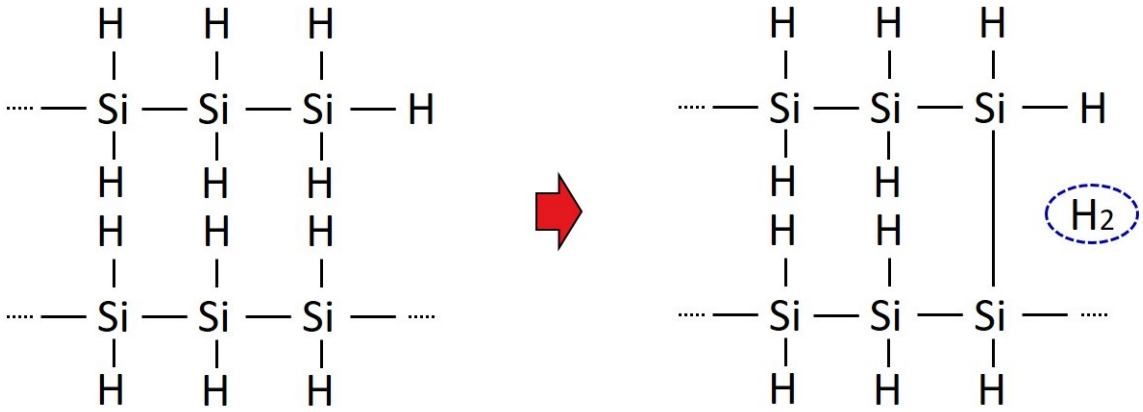


Fig. 6 Proposed model of the cross-linking reaction of polysilane with H_2 elimination process[4].

The relationship between pattern transferability of silicon gel by nanoimprint and the network structure is discussed here. According to a report written by Masuda et al., no patterns were obtained on gel films prepared at 100°C, whereas well-defined patterns were imprinted on the film prepared at 140°C–180°C. Also, no patterns were obtained on gel films prepared at 220°C. Thus, drying temperature of silicon gel affects the imprint properties of the films. Here we compare the results of wet etching and patter transferability from 150 to 180°C. After wet etching, the network structure appeared at 100°C, and it grew with drying temperature from 100°C to 150°C followed by it developed most at 180°C. Well-defined patterns were obtained at 150–180°C. This temperature range (150–180°C) corresponded with the temperature range that silicon network develop the most in Fig. 4. Therefore, the development of the networked silicon structure would affect the

deformability of the silicon gel.

4. Conclusion

Pressure-induced phase separation was observed in gel films, indicating the existence of fluctuation in the gel. Two fluctuation modes appeared and developed as spinodal decomposition under pressure condition. The experiment of partial dissolution of the gel also emphasized the two phases in the film. FTIR measurement gives a model that these two phases is interpreted as networked silicon structure and isolated polysilane phase. The development of the networked silicon structure would directly affect the imprint properties of the film. The network structure in the gel film developed from 100°C to 180°C followed by it disappeared at 220°C. Similarly, the imprint properties (embossing properties and deformability) of the gel film improved from 100 to 180°C followed by it disappear at 220°C. We concluded that the liquid-to-solid conversion in liquid silicon film pass through the gel state that contain two phase: closs-linked silicon network and isolated polysilane. Moreover, 180°C as drying temperature was appropriate condition for imprinting of the film because networked structure develops most at this temperature. Based on these findings, we obtained well-defined silicon patterns via direct imprinting of liquid silicon.

References

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