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| Title | 液体Siインクを用いたアモルファスシリコン薄膜の形成技術とその反応機構 |
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Silicon thin films are key components of most semiconductors and can be fabricated from hydrosilanes ($Si_xH_y$). In most cases, Si films are fabricated by chemical vapor deposition (CVD) method using precursor of $SiH_4$ gas or $Si_2H_6$ gas with costly vacuum process. In contrast, by using precursor of "liquid-Si ink" prepared by photopolymerization of cyclopentasilane ($Si_5H_{10}$) or cyclohexasilane ($Si_6H_{12}$), Si films can be fabricated by a simple coating method without vacuum process. The liquid-Si ink can be converted to Si films by heating to 350 °C or higher.

However, the mechanisms of photopolymerization and thermal reaction of cyclosilanes had not been clarified. The molecular weight of general silicon compounds decreases with UV light irradiation. Exceptionally, the molecular weight of the cyclosilanes increases with UV light irradiation. There was the problem of poor reproducibility of photopolymerization of cyclosilanes, and the cause was unknown. Therefore, the photopolymerization of cyclosilanes had been carried out while adjustments every time. Clarification and control of photopolymerization were indispensable for practical application of liquid-Si ink. Also, the thermal reaction of hydrosilanes had been studied in many studies, but most of them were directed to high temperature about 400 °C or higher, and thermal reaction at low temperature was unexamined. In order to improve the storage stability of liquid-Si ink, it was required to analyze thermal reactions of cyclosilanes around room temperature.

In this study, we examined the following matters. (1) analysis of photopolymerization of cyclosilanes and proposal of new reaction mechanism, (2) analysis of thermal reactions of cyclosilanes and calculation of the activation energy, (3) analysis of change with time of liquid-Si ink by using gel permeation chromatography and the Hamaker constant, (4) calculation of intermolecular forces of hydrosilanes, (5) preparation of amorphous Si films by the slot-die coating method with liquid-Si ink.

The following results were obtained from this study. (1) With the new photopolymerization mechanism composed of 4 elementary reactions, we were able to explain the results of previous experiments. In addition, we succeeded in improving reproducibility of photopolymerization by changing conditions based on the new reaction mechanism. (2) In the thermal reaction, it was found that the dimer was formed first, and the oligomer was gradually formed. The calculated activation energies of cyclopentasilane and cyclohexasilane are 174 and 184 kJ/mol, respectively. (3) Polyhydrosilanes with large molecular weight (>$10^5$ g/mol) are found to form aggregates and these aggregates can be dissociated by adding strongly attached solvents. (4) The intermolecular force of hydrosilane increases rapidly with increasing molecular weight. (5) The a-Si films were obtained with less material loss by the simple procedures.

As a result of this research, details of liquid-Si ink have been elucidated and handling is facilitated. We gained knowledge to be the foundation of application development of liquid-Si ink in the future.

**Keywords:** liquid silicon ink, cyclopentasilane, cyclohexasilane, polyhydrosilane, intermolecular force, Hamaker constant, slot-die coating method