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Preparation and Properties of Thin Films of Polysilane Copolymers, Poly(Dimethylsilylene-*Co*-Methyl-*n*- Propylsilylene)s

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Oriented thin films and unoriented thin films of polysilane copolymers, poly(dimethylsilylene-*co*-methyl-*n*-propylsilylene)s, were prepared by friction transfer and solution cast method, and their properties were compared with each other. There were two solid states in the polysilane copolymers at room temperature. One is the stable phase, which absorbs the light around 300nm and emits the light at 360nm. Another is the metastable phase, which has the absorption band around 340nm and the fluorescence at 355nm.

Keywords: polysilane; orientation; thin film; optical properties

INTRODUCTION

Polysilanes are promising materials for opto-electronic devices. We have already reported that highly oriented thin films of insoluble polysilanes, such as poly(dimethylsilylene) (PDMS) and poly(diethylsilylene), could be prepared by friction transfer technique [1-3]. It was found that these films had specific optical properties, which were different from powder sample[4]. For example, the peak in photoluminescence (PL) spectrum of the oriented thin film was

observed at higher energy than that of powder sample. In this study, oriented thin films and unoriented thin films of polysilane copolymers, poly(dimethylsilylene-*co*-methyl-*n*-propylsilylene)s, were prepared by friction transfer and solution cast method, and their properties were compared with each other.

EXPERIMENTALS

Copolymers were synthesized by Wurtz coupling of the mixture of two monomers, dimethyldichlorosilane and methyl-*n*-propyldichlorosilane, with sodium metal[5]. The composition of the copolymers were almost same as that of the fed monomers. Oriented thin films of polysilanes were made by friction transfer technique[3], as follows. Pellet of polysilane was pressed on the smooth substrate with constant pressure, and it was slid straight along an direction on the substrate, whose temperature was controlled. Then, thin film of polysilane was formed on the substrate. Cast films were made from the solution of hot tetrachloroethane.

RESULTS AND DISCUSSION

Oriented thin films of the copolymers could be prepared by friction transfer technique. Especially, copolymers which were mainly composed of dimethylsilylene units (90%, 80% or 70%) afforded highly oriented thin films with good quality at lower substrate temperature than the case of PDMS. Figure 1 shows polarized absorption spectra of the oriented thin film of a copolymer composed of 90% dimethylsilylene units and 10% methyl-*n*-propylsilylene units (MMMP91), which was prepared at 180°C. On the other hand the polysilane copolymers were soluble in tetrachloroethane over 90°C, and cast films could be prepared from the solution. The absorption

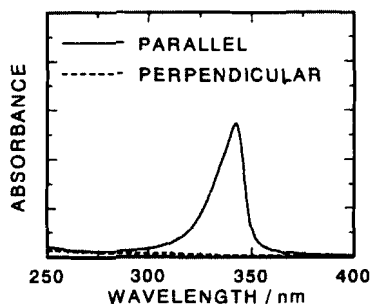


FIGURE 1. Polarized UV spectra of copolymer MMMP91.

spectra of the cast films had two absorption peaks. After annealing at 200°C under vacuum, the absorption peak at the lower energy diminished, and photoluminescence was shifted to lower energy. Figure 2 reveals the change of absorption spectra of the cast film of MMMP91 before and after annealing, and the spectrum of the film friction-transferred at 160°C .

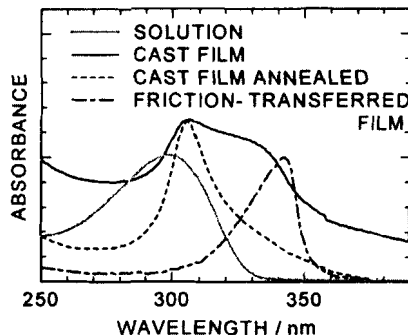


FIGURE 2. UV spectra of MMMP91.

Figure 3 exhibits the PL spectra of the copolymer MMMP91 in various states. PL spectra of the oriented thin films were shifted to the shorter wavelength from those of bulk sample, as was observed in PDMS[4].

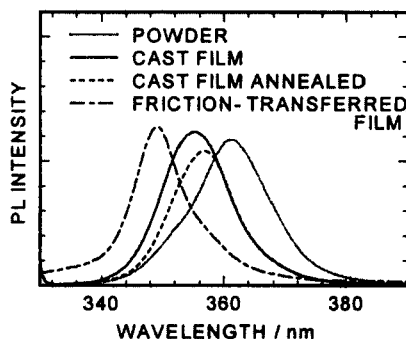


FIGURE 3. PL spectra of MMMP91.

Roughly speaking, there were two solid states in the polysilane copolymer at room temperature. One was the stable phase, which absorbed light around 300nm and emitted light at 360nm. Another was the metastable phase, which had an absorption peak around 340nm and had photoluminescence at 355nm. Two states co-existed in the as-cast films, but the metastable phase was irreversibly transformed into the stable phase by annealing. However, the friction-transferred films were mainly composed of the semi-stable phase, which were highly ordered and not decreased by annealing. Almost all of the powder sample consisted of the stable phase.

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