Preparation and Dielectric Property of Photo-Curable Polysilsesquioxane Hybrids

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1. Introduction

Organic thin-film transistors (OTFTs) have been extensively studied for many advantages such as flexibility, light weight, and low cost, so on.\textsuperscript{1,2} If organic materials can be used to fabricate TFT devices instead of amorphous silicon (\(\alpha\)-Si:H), many application will be expected for the electronic paper, smart card, and electronic identification tags, so on.

Although the most of researchers have enthusiastically investigated the printable organic semiconductors for OTFTs, there are some problems to use the conventional gate insulator relative to the impressive progress of organic semiconductor for the practical application.

It is necessary to develop the gate insulator, which can be fabricated by easy and inexpensive solution-process. Polymeric materials are considered candidates for the gate insulator instead of the thermally grown silicon dioxide. Therefore, we have investigated the synthesis of polysilsesquioxane (PMSQ), its application to the gate insulator, and the evaluation of TFT performance based on polysilsesquioxane gate insulator.\textsuperscript{3}

2. Experimental

The gate insulator with photolithographic properties will give many advantages of designing various TFT devices. And also, it is necessary to develop patternable and low-temperature processable organic gate insulator.\textsuperscript{4,5} We focused our efforts on patternable polysilsesquioxane films, which can be fabricated by spin-coating and low temperature process. In this work, photo-curable polymethylsilsesquioxane hybrids are synthesized by a sol-gel method with acryl groups. Schematic illustration for the preparation of hybrid films is shown in Figure 1.

When the polycondensation of methyltrimethoxysilane (MTS) and acryloxypropyltrimethoxysilane (APTS) was carried out at 70 °C, insoluble substances were generated. This indicates the acryl group may be polymerized due to the thermal radical polymerization. To avoid the polymerization, we conducted the synthesis of polysilsesquioxane at lower reaction temperature (50 °C), then the stable polymethylsilsesquioxane PMSQ-Acryl solution was obtained. The molecular weight of PMSQ-Acryl was affected by the molar ratio of the two monomers (MTS and APTS). In the case of PMSQ-Acryl 2, the low molecular weight polysilsesquioxane was yielded due to the high content of APTS as shown in Table 1.
3. Results and Discussions

The PGMEA solution of PMSQ-Acryl 1 with Darocure 1173 (10wt% relative to PMSQ-Acryl) as a photo-radical initiator was spin-coated on the glass substrates and the films were exposed to UV light by a high pressure Hg lamp (80 mW/ cm²), which is abbreviated as P-PMSQ-Acryl 1. The photopolymerization of PMSQ-Acryl 1 was confirmed by Raman spectroscopy. In the Raman spectrum of P-PMSQ-Acryl films, the peaks at 1640 and 1420 cm⁻¹ assigned to the acryl group were disappeared, indicating the photopolymerization of the acryl groups. The distinct changes can be observed in Raman spectra compared to FT-IR spectra.

The PMSQ-Acryl 1 is a negative-type resist, which were not dissolved in 2-propanol after UV exposure. This indicates the PMSQ-Acryl 1 films can be applied to photolithographic process. The thin film of PMSQ-Acryl 1 with Darocure 1173 were exposed to UV light through a photomask, then the 250 µm L&S negative-patterns were obtained by the development with 2-propanol. At this moment, the FT-IR spectra indicated that a lot of silanol remained in the film. However, these films were heated at 100 °C for 1 h, then 150 °C for 1 h, and polysilsesquioxane hybrid gel films were formed by the polycondensation reaction of the silanol. Therefore, it is found that photo-curable polysilsesquioxane hybrids can be patternable materials.

On the other hand, the requirement for gate insulator of OTFTs are high resistivity and pinhole-free thin-film formability. According to the literature, polymer gate insulator should preferably have no dependence of dielectric constant by changing the frequency. We previously reported that PMSQ was an useful material as the gate insulator for OTFTs. In PMSQ film, the dielectric constant was not changed even at a higher temperature. This indicated that PMSQ film contain low ionic impurities. The dielectric constant of polysilsesquioxane gel films was measured by impedance analyzer (solatron). In this system, it is expected that the decomposed substances of photoinitiator would act as ionic impurities. However, it is found that the decomposition of Darocure 1173 did not generate ionic impurities.

Photo-cured P-PMSQ-Acryl 1 films, which were prepared by photo-radical polymerization using Darocure 1173, showed higher resistivity than PMSQ-Acryl 1 film as shown in Table 1. These results showed that the low resistivity with the existence of acryl group. Indeed, PMSQ-Acryl 2 also showed also lower resistivity than PMSQ-Acryl 1 films.

The film morphology was measured by atomic force microscopy (AFM), P-PMSQ-Acryl 1 films showed the smooth and pinhole-free surface (not shown data). This observation indicates that P-PMSQ-Acryl 1 films possess one of requirements for the gate insulator of OTFTs.

In summary, we have developed the photopatternable polysilsesquioxane, which is introduced the acryl groups to PMSQ. These organic-inorganic hybrid films showed the high resistivity over 10¹⁴ Ωcm and the smooth surface. These materials would be useful gate insulators for the organic TFTs.

Table 1. Results on the preparation and the dielectric property of PMSQ-Acryl

| MTS: APTS | Mwᵃ | Mw/Mnᵇ,c | Resistivity / Ωcmᶜ,d | PMSQ-Acryl 1 x=0.8, y=0.2 | 5.3 | 1×10⁻¹⁴ |
| P-PMSSQ-Acryl 1 | 0.8:0.2 | 4300 | 2.31 | 5.2 | 5×10⁻¹⁴ |
| PMSQ-Acryl 2 x=0.5, y=0.5 | 0.5:0.5 | 3000 | 1.83 | 5.4 | 2×10⁻¹³ |

ᵃ) Estimated by GPC in THF using polystyrene standards.
b) Baking temperature: 100 °C for 1h and 150 °C for 1h.
c) Measured at 1 kHz.

de) Measured at 1 kHz.

References