High Refractive Index Photo-sensitive Siloxane Coatings

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Electronic devices equip several optical devices such as displays, touch sensors, image sensors (cameras), etc. A lot of kinds of clear coatings are used as important components for the devices. We studied to fuse inorganic nano-filler with siloxane, and developed novel clear coating “PF-series” with heat resistance, high refractive index, and positive photo-sensitivity. We succeeded in grafting siloxane to nano-filler with high refractive index, and the film showed excellent heat and optical stability. Also we designed the siloxane coatings to photosensitize, so photo-positive patterning was enable. These features will promise that PF-series are suitable for the optical device application.

Keywords: High refractive index, Heat stable, Photosensitive, Transparent, Siloxane

1. Introduction

The image sensors are applied as the camera for the various kinds of electronic devices such as mobiles, tablet type devices, digital cameras, laptops, car sensors and so on (Fig. 1). Recently photo detective area of those CCD and CMOS sensors are becoming smaller due to requirements of fine pixel resolution and fine feature size. In order to obtain higher sensitivity, light should be focused on its photo detector area in the sensor. To concentrate the light, fabricating micro-lens on the photo detective area is being investigated [1]. High refractive index (R.I.) compound is desired to make effective lens. However, usual organic coatings, such as polyimides and acrylic polymers, do not have high enough refractive index, and have problems with either transparency or heat stability. Therefore, the inorganic materials, like silicon nitride and titan oxide, are appropriate for that use, but their film highly cost to form because of chemical vapor deposition process.

The micro-lens is regularly obtained by following dry-etching processes; coating of the lens layer on the color filter, patterning and reflowing of the posi-resist formed on the lens layer, and etching of the both resist pattern and lens layer by plasma gas (Fig. 2).

The lens layer is preferred to be homogeneous material because we could get smooth surface on the lens at dry-etching. Smooth surface is desired for effective lens. In order to get high refractive index, it is generally considered to combine organic polymer with inorganic compounds like nano-filler. However, if the lens layer consists of the mixture with organic polymer and inorganic materials, rough lens will be definitely formed at dry-etching because of different etching rate between organic and inorganic.

Then, we focused on poly-siloxane, which is organic / inorganic hybrid material with similar
etching rate to inorganic compounds, excellent transparency and heat resistance. We studied to fuse inorganic nano-filler with poly-siloxane, and succeeded in grafting poly-siloxane to the nano-filler.

As a result, we achieved forming the film which has transparency, heat resistance and higher refractive index than 1.7 at 550 nm wavelength.

Furthermore, we performed compatibilization of siloxane by the molecular design with the naphthoquinonediazide compounds, and pattern processing of the positive type photosensitivity was enabled.

In this way, we developed high refractive index photo-positive siloxane coatings “PF-series” with good transparency at visible wavelength range and heat stability [2]. In this paper, we introduce its novel materials.

2. Experimental

2.1. Synthesis of siloxanes

We synthesized two types of siloxane, of which one grafted to nano-filler and the other did not. The grafting poly-siloxane was synthesized by hydrolyzing and partially condensing organosilanes (Shin-Etsu Chemical Co., Ltd.) with aromatic group and alkali soluble group in presence of the nano-filler. The nano-filler was composed of titanium oxide mixture (JGC Catalysts and Chemicals Ltd.), which had high refractive index and its average grain size was 15 nm. On the other hand, the siloxane without grafting was obtained by hydrolyzing and condensing their organosilanes.

2.2. Analysis of siloxanes

2.2.1. Gel permutation chromatography

Molecular weight of the siloxane was measured by TOSOH HLC-8220 GPC in THF solution, and determined using Polystyrene as standard.

2.2.2. FT-IR measurement

FT-IR measurement was carried out by KBr method (HORIBA FREEACT-II FT-720). The sample was prepared by following procedure.

The solution of the poly-siloxane with nano-filler was located in centrifugal separator. After nano-filler was removed from siloxane solution, solvent was removed under reduced pressure to give white powder.

2.3. Preparation of the siloxane coating

We blended the poly-siloxane, the photosensitizer, and solvent in the vial container, and then they were dissolved uniformly by shaking for few minutes. We used the mixture “PF-3500” as the siloxane coatings.

The component of PF-3500 is shown in below table (Table 1). The grafting poly-siloxane was applied for PF-3500. All compounds except for the polymers were purchased and provided from chemical manufactures and used for experiments without further purification.

| Type          | Component                                               |
|---------------|---------------------------------------------------------|
| Polymer       | Grafting poly-siloxane with nano-filler                |
| Photosensitizer| Naphthoquinonediazide compound                         |
| Solvent       | Propyleneglycol monomethylether acetate, Diacetone alcohol |

2.4. Patterning processes and evaluation

The polymer film was spin-coated on 8 inch Si wafer using a solution of PF-3500 with a spin coater, and baked on a hot plate (100 °C for 180 sec, Tokyo-electron Mark-7).

After exposure to UV radiation through a reticle by NSR2009i14 i-line stepper, the wafer was rinsed with 2.38% aqueous solution of tetramethylammonium hydroxide (TMAH) for development. The thicknesses of the film were about 1-1.5 μm.

After baking, thickness was measured by STM-802 (Dainippon Screen MFG).

The baked wafer was exposed by broad band aligner (Canon PLA-501) with 1000 mJ/mm² (at 365 nm) through a gray-scale mask.

After the development, thickness was measured by STM-802. The developed wafer was treated at 220 °C for 5 min as post baking.

2.4.1. Scanning electron microscopy (SEM: S4800)

SEM measurement was carried out after curing the developed wafer to obtain cross-sectional view of lithographic pattern.

2.4.2. Refractive index and transparency measurement

Ellipsometer ”FE-5000” (Otsuka) was used to measure the refractive index (R.I.) and extinction coefficient (k-value). Transmittance was calculated by the k-value.

2.5. Reliability evaluation

2.5.1 Heat resistance test

The cured PF-3500 film was heat-treated by 250 °C for 10 min on hot plate, and 150 °C for 1000 h in heat chamber (Espec corp. SU-241). Then the treated film was measured R.I. and k-value.
2.5.2. Heat and humidity resistance test

The cured PF-3500 film was treated under the condition of 85 °C 85% in heat and humidity chamber (Espec corp. SH-222) for 1000 h. Then the treated film was measured R.I. and k-value.

2.5.3. Thermal-cycle test

The cured PF-3500 film was treated for 300 cycles at a circulation heating from -55 °C to 125 °C in heat chamber (Espec corp. SU-241). Then the treated film was measured R.I. and k-value.

2.5.4. Heat stable evaluation

Thermal gravimetric apparatus TGA-50 (Shimadzu Corporation) was used to measure a weight change at a heating rate of 10 °C/min up to 400 °C in nitrogen atmosphere 1% and 5% weight loss temperature of PF-3500 was determined.

3. Results and discussion

3.1. Grafting siloxane to inorganic nano-filler

Grafting poly-siloxane showed higher molecular weight than the siloxane polymer without filler (Fig. 3). The result indicated that poly-siloxane was fused to nano-filler and detected as huge molecule. We confirmed that siloxane bonding was formed in the isolated powder of nano-filler by FT-IR measurement (Table 2). Then we suggest that poly-siloxane grafts to nano-filler as below image (Fig. 4).

![Fig. 3. GPC traces of different siloxanes.](image3)

![Table 2. IR absorptions detected in isolated powder of nano-filler.](table2)

| Bonding   | IR shift (cm⁻¹) |
|-----------|-----------------|
| -Si-O-Si- | 1098            |
| -Si-OH    | 910             |
| -Si-C-    | 1271            |

3.2. Photolithographic properties

As shown in Fig. 5, the PF-3500 showed the sensitivity of 83 mJ/cm² and large gamma-value of 5.6. That meant higher contrast between before and after developing. Therefore, the good pattern profile and fine resolution were observed by SEM measurement (Fig. 6).
3.3. Optical properties evaluation

No change of optical properties by heating is one of the most important factors for the materials to apply into the optical devices. Therefore, we investigated the change of refractive index and transparency in PF-3500 coating after various heating conditions (Table 3). As a result, PF-3500 was found to show more than 95% of transparency in wavelength range of 400-800 nm, and little change after each heat condition. Refractive index was also hardly changed. Therefore, the cured PF-3500 was considered to have excellent heat stability.

| Table 3. Optical property of PF-3500. |
|------------------------------------|
| **sample** | Wavelength (nm) | R.I. | Extinction Coefficient (k-value) | $\%T$ $^1$ /1μm |
|-----------|-----------------|------|-------------------------------|-----------------|
| Before test | 400 | 1.876 | 8.02×10$^{-4}$ | 97.5 |
|  | 550 | 1.791 | 0.00 | 100 |
|  | 633 | 1.775 | 0.00 | 100 |
| After 250 °C 10min | 400 | 1.869 | 1.07×10$^{-3}$ | 96.7 |
|  | 550 | 1.785 | 0.00 | 100 |
|  | 633 | 1.768 | 0.00 | 100 |
| After 150 °C 1000h | 400 | 1.868 | 8.53×10$^{-4}$ | 97.4 |
|  | 550 | 1.785 | 0.00 | 100 |
|  | 633 | 1.769 | 0.00 | 100 |
| After thermal cycle test | 400 | 1.902 | 1.06×10$^{-3}$ | 96.7 |
|  | 550 | 1.811 | 0.00 | 100 |
|  | 633 | 1.794 | 0.00 | 100 |
| After 85°C 85% 1000h | 400 | 1.907 | 1.06×10$^{-3}$ | 96.7 |
|  | 550 | 1.815 | 0.00 | 100 |
|  | 633 | 1.798 | 0.00 | 100 |

$^1$ Calculated by following formula: $T\% = \exp (-4\pi k / \lambda \times (1.0 \times 10^{-6})) \times 100$, k: extinction coefficient, $\lambda$: wavelength.

3.4. Heat stability evaluation

1% and 5% weight loss temperatures are important indexes to evaluate heat stability. According to the results shown in Table 4, PF-3500 after curing at 220 °C was found to show higher weight loss temperature than usual transparent coatings composed of acrylic polymers. Consequently, cured PF-3500 had excellent heat stability.

| Table 4. 1% or 5% weight loss temperature of PF-3500. |
|-----------------|-----------------|-----------------|
| Sample | Temperature (°C) | 1% weight loss | 5% weight loss |
| PF-3500 | 286 | >400 |
| Conventional acrylic coatings | 275 | 322 |

4. Conclusion

We developed the high refractive index photo-positive siloxane coatings “PF-series”. The coatings had good photolithographic performance, excellent transparency and heat stability. Therefore, PF-series might be promising good performance for the optical devices.

References
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