Organic-Inorganic Hybrid Materials for UV-Nanoimprint Lithography

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We developed the organic-inorganic hybrid material for UV-nanoimprint lithography (UV-NIL). Silicasol particles were used as inorganic component and modified their surface with photosensitive crosslinkers. These photosensitive silicasol particles were dispersed uniformly into photosensitive monomers with non-solvent systems. They were mixed with other monomers and photoinitiator to prepare various imprint materials. Physical properties and mechanical properties of these materials were examined. The UV-NIL patterns were obtained by using an imprint test machine “LTNIP-5000” from Litho Tech Japan Co. The results showed greatly improved UV hardening properties and physical properties such as refractivity, thermal stability compared to organic (non-hybrid) materials. As a result, 200 nm line and space patterns were successfully imprinted with no shrinkage at pressure of 3.1 MPa and exposure doses of 1 J/cm².

Keywords: UV-NIL, organic-inorganic hybrid materials, silicasol, nanoparticles, monomer substitution

1. Introduction
There are numerous methods of next generation lithography (NGL) technology to obtain below 100 nm size. NIL technology has one of the most promising NGL technologies because of its wide range lithography performance and good cost performance [1, 2]. On the other hand, it has also been indicated that the selection of materials has been a key issue due to their large application fields of this technology.

We have been developing photosensitive materials using organic-inorganic hybrid materials. By hybridization of the inorganic nanoparticles with organic polymers, it is possible to obtain a new material having both advantages of organics and inorganics. Our former research revealed that the introduction of inorganic nanoparticles, especially containing photosensitive groups on their surfaces, into i-line or KrF photoresists improved their resolution and RIE resistance [3].

In this research, we selected colloidal silica as an inorganic material and dispersed it uniformly into various monomers with non-solvent system. We also evaluated them as organic-inorganic UV Nanoimprint materials.

Dispersed silicasols are also treated with photosensitive crosslinkers in order to improve the UV hardening performance and various physical properties, especially thermal stability. This photosensitive silicasol distributed monomer has been formulated with other monomers and various imprint materials were prepared. The UV-NIL performance was tested using LTNIP-5000 of Litho Tech Japan Co. and 200 nm line and space patterns were successfully imprinted with our organic-inorganic hybrid materials.

2. Experimental
2.1. Preparation of UV-NIL materials and measurement of physical property
2.1.1. Preparation of inorganic particles (colloidal silica) having photo-functional groups
As the inorganic particles having functional groups, a colloidal silica was treated with acryloxypropytrimethoxysilane (KB5103, manufactured by Shin-Etsu Chemical Co., LTD.). The colloidal silica which is treated with acryloxypropytrimethoxysilane was prepared by adding 135 g of acryloxypropytrimethoxysilane...
and 1050 g of isopropanol to 450 g of silica particles (organosilicasol, manufactured by Nissan Chemical Industries, LTD, under the trade name Snowtex, IPA-ST, colloidal silica-in-isopropanol solution with a solid content of 30 % by weight and a mean particle size of 10 to 20 nm) and acid catalyst. The mixture was stirred at room temperature for 24 hours to introduce photosensitive groups onto the surface of the silica particles. As a result of analyzing the silicasol solution after a reaction by Gas Chromatography, no reacted coupling reagent was detected. It was also analyzed that the reaction speed can be changed by the amount of catalyst. These results indicate that silane-coupling reagent was reacted onto the silica sol surfaces.

2.1.2. Monomer substitution

The solvent of prepared inorganic particles having photo-functional groups was substituted by monomers. UV-NIL materials were required to be non-solvent systems because there is no exit of vaporized solvents during the UV-NIL process.

The monomer substituted silicasol having photo-functional groups was prepared by adding 45 g of mono-functional acryl monomer and stirring sufficiently. The mixture was distillated under a reduced pressure condition. We found that the particle size of silicasol was not changed after the substitution by monomers. We also found that the particle size and viscosity are stable after 5 months storage at room temperature. These results indicates that the photofunctional silicasol stably and uniformly exist in monomers of non-solvent systems.

As in the case of silicasol having photofunctional groups, non-photofunctional silicasol, that is organosilicasol IPA-ST itself, IPA was substituted to mono-functional monomer. However, during the substitution process, organosilicasol were aggregated together. According to this result, mono-functional monomer was changed, but in this case, silicasols were aggregated after substitution.

These results indicated that, acryloyloxypropyltrimethoxysilane, which crosslinked with silicasols plays a role as a dispersant, then, photofunctional silicasols were dispersed uniformly in to mono-functional monomers.

2.1.3 Formulation of UV-NIL materials

Among various kinds of polymerizable monomers, we chose three monomers such as mono-functional acryl monomers, bi-functional methacryl monomers and tri-functional acryl monomers. These monomers were mixed with photofunctional silicasol and radical type photoinitiators under various proportions. The prepared UV-NIL materials are shown in Table 1 and Figure 1.

![ Radical type photoiniator (Darocure4265 manufactured by Ciba Specialty Chemicals K.K. Japan) ]

Total 13 samples were prepared. KRP-01, KRP-05, KRP-10, KRP-11 and KRP-13 are mixtures without photofunctional silicasol samples. KRP-12 is a photofunctional silicasol dispersed monomer solution itself.

2.1.4 Viscosity measurement

It is known that the viscosity of UV-NIL materials affects to performance of imprint. Viscosities of formulated samples were measured by vibration viscometer (Viscomate VM-1G-L, YAMAICHI electronics).

2.1.5 Refractive index measurement

Refractive indexes of these samples were measured by an Abbe Refractometer (Abbe refractometer DR-M2, Atago Co. LTD.).

2.2 Mechanical property measurements

2.2.1 Thermogravimetric Analysis (TG analysis)

Thermo gravimetric analysis was performed to investigate the thermal stability of the UV cured materials. The samples for the measurement were prepared as follows. A drop of sample was put on the slide glass and covered with another glass with 50 μm gap. It was exposed with UV light. After removing the cover glass, sample film was peeled off from another side of glass. TG analysis was performed on a Thermo plus TG 8120 at a heating rate of 10 °C min-1 under nitrogen atmosphere. In this study we defined the thermal stability as two temperatures at which the weight reduces by 5 % and 20 %.


**Table 1. List of UV-NIL materials**

<table>
<thead>
<tr>
<th>sample name</th>
<th>photofunctional silicasol</th>
<th>Mono-functional acryl monomer</th>
<th>Tri-functional acryl monomer</th>
<th>Di-functional methacryl monomer</th>
<th>Viscosity (cP)</th>
<th>Refractivity @598nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRIP-01</td>
<td>0</td>
<td>50</td>
<td>50</td>
<td>0</td>
<td>10.4</td>
<td>1.4583</td>
</tr>
<tr>
<td>KRIP-02</td>
<td>5</td>
<td>45</td>
<td>50</td>
<td>0</td>
<td>14.4</td>
<td>1.4588</td>
</tr>
<tr>
<td>KRIP-03</td>
<td>10</td>
<td>40</td>
<td>50</td>
<td>0</td>
<td>23.2</td>
<td>1.4602</td>
</tr>
<tr>
<td>KRIP-04</td>
<td>15</td>
<td>35</td>
<td>50</td>
<td>0</td>
<td>38.4</td>
<td>1.4626</td>
</tr>
<tr>
<td>KRIP-05</td>
<td>0</td>
<td>50</td>
<td>25</td>
<td>25</td>
<td>6.39</td>
<td>1.4540</td>
</tr>
<tr>
<td>KRIP-06</td>
<td>5</td>
<td>45</td>
<td>25</td>
<td>25</td>
<td>8.29</td>
<td>1.4547</td>
</tr>
<tr>
<td>KRIP-07</td>
<td>15</td>
<td>35</td>
<td>25</td>
<td>25</td>
<td>17.5</td>
<td>1.4592</td>
</tr>
<tr>
<td>KRIP-08</td>
<td>22.5</td>
<td>52.5</td>
<td>12.5</td>
<td>12.5</td>
<td>9.70</td>
<td>1.4486</td>
</tr>
<tr>
<td>KRIP-09</td>
<td>27</td>
<td>63</td>
<td>5</td>
<td>5</td>
<td>6.80</td>
<td>1.4428</td>
</tr>
<tr>
<td>KRIP-10</td>
<td>0</td>
<td>90</td>
<td>5</td>
<td>5</td>
<td>2.09</td>
<td>1.4373</td>
</tr>
<tr>
<td>KRIP-11</td>
<td>0</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>1.74</td>
<td>1.4332</td>
</tr>
<tr>
<td>KRIP-12</td>
<td>30</td>
<td>70</td>
<td>0</td>
<td>0</td>
<td>5.48</td>
<td>1.4397</td>
</tr>
<tr>
<td>KRIP-13</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>100</td>
<td>17.9</td>
<td>1.4679</td>
</tr>
</tbody>
</table>

Unit: weight %  Every mixture include 1.25 weight% DAROCURE4265.

2.3 Property for UV-NIL process

2.3.1 Simplified method of mold peeling

In the process of UV-NIL, mold separation is one of the key issues. In this paper we have tried the novel simplified method for mold peeling capability. Slide glasses were treated with 1 % Optool DSX / Demnum solvent solution (Daikin Industries, LTD.) using a dipping method. Contact angle of Optool treated glass was 112 ° and these glasses were used as a mold. On the other hand, other glasses were dipped in H₂SO₄ and rinsed with pure water. We also applied spin coating of HMDS (Hexa Methyl Disilazane) to the glasses. These glasses were used as a substrate. The contact angle of H₂SO₄ treated glass was below 10 ° and HMDS treated glass was about 30 °.

A drop of prepared UV-NIL material was put on the substrate (slide glass), a H₂SO₄ treated glass or a HMDS treated glass, and covered with Optool treated glass with 50 μm gap and exposed with UV light for 1 J/cm² at 365 nm. After cured by UV light, Optool treated glass was removed manually. We checked the UV cured membrane was attached whether to a substrate glass or to Optool treated glass. On each sample, 5 runs were tested. This test was named as “Peeling Test”.

2.3.2 Pattern transfer by UV-NIL

Pattern transfer experiment has been done after the check of simplified method of mold peeling. The UV-NIL performance was obtained by using an imprint test machine LTNIP-5000 at the pressure of 3.1 MPa and exposure doses of 1 J/cm². LTNIP-5000 could imprint both thermal and UV mode which is manufactured by Litho Tech Japan Co.

3. Results and Discussion

3.1 Physical property of UV-NIL materials

3.1.1 Viscosity

The material for NIL was required to have a low viscosity because of pattern transfer and thickness of residual film. In this study, mono-functional acryl monomer was selected as a substituted monomer for photofunctional silicasol. KRIP-14 is mono-functional acryl monomer itself and its viscosity was very low, 1.74 cP (described in Table 1.). Viscosity of KRIP-12, photofunctional silicasol dispersed monomer itself, shows higher viscosity compared to the monomer itself, in fact, with increasing the concentration of silicasol, the viscosity became higher. Among these samples, KRIP-08 showed low viscosity even though it includes high concentration of silicasol, 22.5 %. This is because the proportion of the mixing monomers was different from other samples, that is, the amount of low viscosity mono-functional monomer was high and amount of high viscosity di-functional monomer was low. These results indicate that viscosity of sample could be controlled by the monomer formulation and silicasol contents.
3.1.2 Refractive index

The same phenomena were observed also in the case of refractive index. Silicasol has thought to have high refractive index 1.52, as same as glass, and refractivity of monomers were around 1.43 to 1.47. Higher silicasol concentration samples show higher refractive index except for KRIP-08. By changing formulation, we can supply UV-NIL materials in accordance with required materials.

3.2 Mechanical property

3.2.1 Thermogravimetric analysis (TG analysis)

In order to investigate the thermal behavior of the prepared sample, organic-inorganic hybrid samples and a sample which consists of only organic component (KRIP-10), the thermal analysis (TG-DTA) was measured. 5% and 20% weight loss temperatures were plotted in Figure 2.

![Fig. 2 Thermal Stability analysis by TG](image)

We can see from KRIP-01 to 04 that both 5% and 20% weight loss temperatures are increasing according to the amount of photofunctional silicasol content. Therefore, the thermal stability was improved when silicasols are included in UV-NIL samples. However, the data of KRIP-05 to 09 show that the silicasol content has no effect on the thermal stability. This is because that, Tg curve of KRIP-10, which consists of mono-functional acrylic monomer, is different from those of other samples (Figure 4). When the thermal stability temperature is defined as the 5% weight loss temperature, KRIP-10 has the best thermal stability among all samples. However, KRIP-10 is drastically decomposed at around 370°C.

TG curve of KRIP-10 was observed to be started to degrade gradually from about 180 °C and to be occurred to decrease quickly from about 350 °C. And the thermal degradation for this sample was suggested to be occurred continuously because of observation of a broad exothermic peak assigned to the thermal degradation from about 180 °C to 400 °C for DTA curve of KRIP-10.

On the other hand, it was found that TG curve of KRIP-05, 06, 07, 08 and 09 were observed to be occurred loosely the weight-loss by thermal degradation. And for DTA curves of these samples, the thermal degradation for these samples was suggested to be occurred intermittently unlike that of KRIP-10 because the plural exothermic peaks were observed in each data.

It was thought that the thermal energy for degradation was contributed to the cleavage of interaction between the hetero-component firstly, and then, the degradation of the organic component started (KRIP-06, 07, 08 and 09).

In addition, it was found that the interaction of the hetero-component was due to the thermal stability, as silicasol content was increasing. The corresponding starting temperature of thermal degradation was tend to increase from the first exothermic peak of DTA curves.

![Fig. 3 TG-DTA Analysis](image)

3.3 UV-NIL properties

3.3.1 Novel simplified method for mold peeling

During the process of UV-NIL, the mold removing from UV-cured material was a key step, because some UV-cured materials behave as adhesive bond and obtained patterns collapse and mold patterns are also damaged [4,5]. Materials
have to tightly be attached to the substrate; on the other hand, the same materials have to be peeled off easily from molds. Therefore, we checked the peeling property of KRIP materials by a novel simplified method as described at 2.3.1. The Optool treated slide glass was used as a mold, and two glasses treated in the different methods which have different contact angle were used as the substrates. For each samples, five run tests were applied. The results are shown in Table 2.

Table 2. Peeling Test

<table>
<thead>
<tr>
<th>treatment</th>
<th>Peeling test</th>
<th>LTNIP-5000 (H₂SO₄ glass)</th>
</tr>
</thead>
<tbody>
<tr>
<td>KRP-01</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>KRP-02</td>
<td>3</td>
<td>5</td>
</tr>
<tr>
<td>KRP-03</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>KRP-04</td>
<td>0</td>
<td>1</td>
</tr>
<tr>
<td>KRP-05</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>KRP-06</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>KRP-07</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>KRP-08</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>KRP-09</td>
<td>5</td>
<td>5</td>
</tr>
<tr>
<td>KRP-10</td>
<td>5</td>
<td>5</td>
</tr>
</tbody>
</table>

Among KRP-01 to KRP-04, no sample could be peeled off from the HMDS glass substrate except KRP-01. The high content of silicasol makes the peeling results worse. However, from the results from KRP-06 to KRP-010, the peeling performance is significantly improved because of adding the bi-functional methacryl monomer which has a flexible structure. Among bi-functional monomer containing samples, KRP-09 which contained 27% silicasol perfectly peeled off from substrate glasses.

All samples were imprinted by LTNIP-5000, KRP-02, KRP-05, KRP-07, KRP-08 and KRP-09 could be removed from a mold successfully. However, KRP-01 and KRP-10 did not show good peeling performance even if the peeling test results were good. Pencil hardness test was supported this conflict. The materials which showed rigid performance or cohesive fraction were not suitable for the NIL materials (the data not shown).

There are several evaluation methods to measure the adhesion force of the samples [6]. These results show that our novel simplified method for mold peeling ability is in good agreement with novel the peeling test results of LTNIP-5000.

3.3.2 Pattern transfer by LTNIP-5000

Figure 4 shows FE-SEM images of KRP materials which shows line and space (L/S=1/1) of 200 nm, 240, 280, 320, 360, 400 nm. Images of KRP-10 in which the lines were not straight and some patterns were peeled off. This is because, UV-cured KRP-10 were very soft, so the patterns were elongated by the forth of a mold removing. The pencil hardness results also supported this phenomenon. KRP-09 also showed some defect and line patterns were little bit elongated and collapsed on to the next line. From KRP-05 to KRP-09, 200 nm lines were satisfactory patterned as in Figure 5, even though they contain the silicasol nanoparticles or not.

Fig. 4 FE-SEM images of various line and space pattern (JSM-6700F, JEOL Ltd)
4. Conclusion

The organosilicasol was treated with photofunctional residues and was dispersed into mono-functional acryl-monomer uniformly. It was formulated with other photofunctional monomers and radical type photoinitiators. Their physical and mechanical properties are so interesting. As a result, we obtained the new types of UV-NIL materials. By hybridization of the inorganic nanoparticles with organic polymers, it is possible to obtain a new material having both advantages of organics and inorganics. These hybrid materials have a high thermal stability and the refractive index controllability by the proper selection and formulation of photofunctional monomers and silicasol. Finally, 200 nm line and space patterns were successfully imprinted even though they contain the silicasol nanoparticles.

And in this research, we can propose the simplified method for a mold peeling capability. This method dose not need special equipment and need no cost.

These results indicate that our new materials can widely be applicable to the new field, such as optical, micro machine and so on. In this study, we have used the silicasol as inorganic materials; however, this technique can be adapted to other inorganic materials, for example, titan, pigment and so on.

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References