Effect of UV Irradiation on Microlens Arrays and Line-and-Spacing Grating Fabricated by Room-Temperature Nanoimprinting Using Organic Spin on Glass

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1. Introduction
Nanoimprint lithography (NIL)\textsuperscript{[1,2]} is beginning to attract considerable attention from many industries because of its potential for producing various nanostructure applications through a simple, low-cost, and high-throughput process. Moreover, with the recent achievement of a high imprint resolution below a few nanometers, there is a consensus forming that supports NIL as the prime candidate for next-generation lithography. There are many polymers that can be used as replication materials in NIL. In particular, sol-gel materials, such as spin-on-glass (SOG) and hydrogen silsesquioxane (HSQ), have useful properties that enable nanoimprinting at room temperature (RT). This means that NIL using these sol-gel materials as the replication material completely eliminates the resist-thermal cycle and UV exposure, which are both prone to causing reductions in pattern accuracy and throughput.

In previous experiments, various RT-NIL processes using SOG and HSQ have been developed, and the processes have produced various nanostructures\textsuperscript{[3-6]}. However, from the viewpoint of device production, it is very important to choose a replication material suitable for fabricating desired applications. For example, micro- and nano-patterns that are used for optical applications require replication materials with sufficient optical properties, including a high refractive index and transparency. The inorganic sol-gel materials that are currently being used as replication materials are also useful as dry etching masks thanks to their sufficient dry-etching durability. However, there is a problem with their optical properties in that they lack refractive index values. Their values are approximately 1.4, which is insufficient for optical applications.

To overcome this problem, in this article we newly propose organic SOG (O-SOG) as a replication material for RT-NIL. O-SOG has a high refractive index of 1.56 and transparency level that exceeds 98\%, which is very efficient for optically practical applications. Figure 1 shows the chemical structure of O-SOG. O-SOG has two different organofunctional groups, \( R^1 \) and \( R^2 \), in the polymer structure instead of the \( H \) groups in the inorganic SOG.

![Fig. 1. Chemical structure of organic spin-on glass.](image)

There are several fabrication techniques for microlens arrays, such as the pattern transfer by etching via a thermal reflow of the resist patterns formed by the lithographic process, and dropping
urable liquid[7,8]. However, these methods are a little complicated and lack the necessary control of the pattern accuracy. In this article, we therefore introduce the fabrication of O-SOG microlens arrays by RT-NIL. The imprinted-microlens arrays need no pattern-transfer processes because of their sufficient optical properties mentioned above.

2. Experiments

First, we measured the IR spectra of an O-SOG resin based on the UV-irradiation time. We used a low-pressure mercury lamp that generates both 185- and 254-nm UV light. As figure 2 shows, a small-sharp peak of Si-OH bonds appeared at 3600 cm\(^{-1}\) in the O-SOG resin without UV irradiation. The peak of the Si-OH bonds increased and shifted broadly to around 3400 cm\(^{-1}\) with the increase in UV-irradiation time. The reason is that the UV irradiation randomly generated the Si-OH bonds, which have a different electron density; hence the peak was shifted and broadly distributed.

Fig. 2. IR spectra of O-SOG resin depending on UV irradiation time.

Increasing the Si-OH bonds indicates that the UV irradiation broke some chemical bonds, such as the Si-O, Si-C, and C-C structures of the resin surface, which means the formation of Si-OH bonds replaced the Si-R bonds. This consequently leads to a reduction of the flow property of O-SOG. Therefore, during annealing, the UV-irradiated patterns maintain their initial profiles due to the low-flow property produced by the UV irradiation. Furthermore, the annealing, at the same time, causes a re-coupling of the broken chemical bonds, which leads to a hardening of the resin.

Then, we measured the annealing temperature dependence of the refractive index of the O-SOG resin. Figure 3 shows the annealing temperature dependence of the refractive index of the O-SOG resin. The O-SOG resin annealed at 100 and 200\(^{\circ}\)C showed the highest refractive index value of 1.56. The values were prone to decrease as the annealing temperature increased, and after 600\(^{\circ}\)C annealing, the refractive index decreased to 1.42. This is attributed to the reduction of the organic principles contained in O-SOG due to annealing. Therefore, we assumed that below 300\(^{\circ}\)C would be a better annealing temperature for maintaining the initial O-SOG patterns profiles without losing the high refractive index.

![Fig. 3. Annealing temperature dependence of refractive index of O-SOG resin.](image)

The following steps are used for the RT nanoimprinting. (1) The O-SOG is spin-coated on a Si substrate. (2) A mold, which is treated by a fluorinated anti-sticking agent (Optool DSX: Demnamsolvent = 1:1000 by weight, Daikin Industries), is pressed into the O-SOG resin at RT. The pressure to produce an accurate imprint replication of a mold ranges from approximately 10 to 50 MPa, which largely depends on shapes of the molds, including the linewidth, pitch, and height. (3) The mold is separated from the O-SOG resin, and then the O-SOG patterns are replicated.
Figure 4 shows the relationship between the imprint pressure and the O-SOG resin thickness.

![Graph showing the relationship between film thickness and pressure required to imprint O-SOG resin.](image)

Fig. 4. Relationship between film thickness and pressure required to imprint O-SOG resin.

We used a 200-nm-high SiO$_2$/Si mold with a 200-nm-line-and-spacing grating for this investigation. There is another useful advantage of O-SOG in that a resin with a thickness above 1 μm can be easily used in single-spin coating. As the results indicate, the pressure decreased as the resin thickness increased. This is due to reduction of deformation resistance of O-SOG-resin surface with an increase in resin thickness[9]. Therefore, increasing the resin thickness offers a lower pressure nanoimprinting, which is very useful for fabricating applications like microlenses, which can ignore the effect of base-layer thickness, even the remaining micron-thick residue after RT nanoimprinting.

Figure 5 shows a scanning-electron microscopy (SEM) micrograph of 2.2-μm-pitch O-SOG microlens arrays imprinted using a microlens array mold made of quartz.

![SEM micrograph of O-SOG microlens array replicated by RT imprinting.](image)

Fig. 5. SEM micrograph of O-SOG microlens array replicated by RT imprinting.

The mold was fabricated by electron-beam lithography and dry etching. The pressure and time for the imprinting were 30 MPa and 1 min, respectively, and the initial resin thickness was 1.4 μm. This indicates that the microlens-array pattern was successfully fabricated by RT imprinting.

Next, we investigated the effect of UV irradiation on the O-SOG-imprinted patterns before annealing. The O-SOG patterns have to be annealed after imprinting to maintain their initial profile, otherwise the pattern deformation gradually progresses due to the inherent flow property. In other words, untreated O-SOG-imprinted patterns become unstable as time elapses. However, the patterns without treatment cannot retain the initial profile after annealing, due to polymer reflow. Figure 6 shows the concrete example of the thermal deformation of the O-SOG-imprinted pattern without any treatment. Figure 6(a) shows a 1-μm-high O-SOG-imprinted pattern of a producing domes with 600-nm diameters. The O-SOG pattern no treated flattened the producing domes into hemispheres after 160°C annealing for 2 min as shown in Fig. 6(b), and they disappeared immediately at an annealing temperature of 200°C.

![SEM micrographs of O-SOG-imprinted pattern without UV irradiation: (a) producing with 600-nm diameters and 1-μm heights, and (b) hemispheres with 1.3-μm diameters and 330-nm heights after 160°C annealing of patterns shown in Fig 6(a).](image)

Fig. 6. SEM micrographs of O-SOG-imprinted pattern without UV irradiation: (a) producing with 600-nm diameters and 1-μm heights, and (b) hemispheres with 1.3-μm diameters and 330-nm heights after 160°C annealing of patterns shown in Fig 6(a).

We previously proposed O$_2$-plasma irradiation on HSQ patterns before annealing to avoid pattern deformation[10]. The O$_2$-plasma-treated HSQ patterns successfully retained their initial rectangular profiles even after 1000°C annealing. However, O$_2$ plasma irradiation is not suitable for O-SOG patterns because they are etched by O$_2$ plasma because the polymer structure contains organofunctional groups. The measured etching rate of O-SOG when subject to O$_2$ reactive-ion etching...
was 10 nm/min. Therefore, we propose UV pre-irradiation for O-SOG patterns before annealing.

Figures 7(a) and 7(b) are AFM images of O-SOG microlens arrays irradiated with UV light before and after annealing at 300°C and the corresponding O-SOG patterns.

Fig. 7. AFM images and corresponding O-SOG patterns of O-SOG microlens array irradiated with UV for 1 min. (a) before annealing and (b) after annealing at 300°C.

The irradiation time was 1 min for each. As Fig. 7(b) shows, the pattern for after annealing had almost the same profile as that before annealing even though patterns without UV irradiation completely disappeared after similar 300°C annealing. This proves the adequacy of using UV irradiation as a pretreatment to prevent the deformation of the O-SOG-imprinted patterns caused by annealing, and thereby making these patterns very useful as the optical devices of microlens arrays.

We also investigated the UV-irradiation effect on the O-SOG patterns of the line-and-spacing grating. Figures 8(a) and 8(b) show UV-irradiated 200-nm-high O-SOG patterns with 200-nm-line-and-spacing grating after 300°C annealing.

Fig. 8. O-SOG-imprinted patterns after 300°C annealing. (a) irradiated 185 + 254 nm UV for 1 min, and (b) irradiated 185 + 254 nm UV for 3 min. The initial resin thickness was 1 μm.

The initial resin thickness was 1 μm. The UV irradiation times were 1 and 3 min, respectively. After annealing, the patterns irradiated with UV for 1 min deformed, as shown in Fig. 8(a). Conversely, the patterns irradiated with UV for 3 min without annealing completely retained their initial rectangular profiles, as shown in Fig. 8(b). These results indicate that there is a dependence on the dose of UV irradiation for maintaining the imprinted-O-SOG patterns after annealing.

In conclusion, we have developed a method for preventing the pattern deformation of O-SOG-imprinted patterns after annealing. O-SOG patterns pre-irradiated with UV light successfully maintained their initial profiles at an annealing temperature of 300°C. This is very suitable for optical applications such as microlens arrays.

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References