UV Nanoimprint Lithography and Its Application for Nanodevices

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Nanostructure fabrication process using ultraviolet nanoimprint lithography (UV-NIL) and electrodeposition were proposed. This method shows remarkable advantages in high throughput production and fabrication cost. For this process, the newly resin which endures wet process was developed. Co dot arrays of 220nm were fabricated by electrodeposition after UV-NIL. GaN structure of 300nm was also realized using Ni as an etching mask fabricated by proposed process.

Keywords: UV-nanoimprint, electrodeposition, magnetic dot array, LED

1. Introduction

There has been an enormous increase in research on ultra-violet nanoimprint lithography (UV-NIL) [1]-[4]. This is a technology for fabricating nanopatterns by imprinting a photocurable resin between a substrate and a mold. This method dispenses with electron beam lithography and dry etching, enabling large-area nanostructure patterns to be produced economically. As a low-cost, mass-production technology, this method is attracting considerable attention. The fabricated nanostructures can be widely applicable for electronics, optics and bionics etc.

In particular, UV nanoimprint has remarkable advantages to thermal heat nanoimprint in the point of throughput, resolution and alignment accuracy. Since thermal cycle necessary for thermal heat nanoimprint is not requested in UV-NIL, accurate shape transfer to the resin from the mold can be obtained. The basic UV-NIL process is shown in Figure 1. Different from conventional lithography technologies, thin residual resin remains on the printed area in the NIL process. The residuals were removed by O₂ RIE. Afterwards, it is possible to fabricate nanopatterns on the substrate by etching with resin mask patterns. On the other hand, the nanometal patterns are formed by electroplating with resin patterns.

First of all, the equipment developed to obtain the UV-NIL process is shown in section 2.1. Then in the section 2.2, the newly developed photocurable resins are introduced. For applications of UV-NIL and electroplating, magnetic dot array and LED are described in section 3.

Fig. 1 UV-NIL process
2. Equipment and Materials
2.1 UV-NIL equipment

Figure 2 shows our newly developed UV-NIL equipment. It consists of a bottom plate to fix a substrate, a top plate to fix the mold, and weight to apply loading force. Pattern defects of air bubble was induced in conventional UV-NIL under atmospheric pressure. To prevent these defects, a vacuum chamber was employed for the newly developed equipment. The cavity formed between the top plate and the bottom plate is hermetically sealed and can be evacuated through the hole in the bottom plate. Imprinting under vacuum avoid bubble contain in the resin. This approach is important for pattern formation in the NIL process.

Fig. 2 Overview and cross sectional structure of the improved UV-NIL equipment

2.2 Photocurable resin

The requested characteristics of the resin can be categorized into two; the characteristics for UV-NIL process and characteristics in actual uses. As a basic process characteristics, spreading, substrate adhesion, non-adhesion with a mold, a low viscosity, velocity stiffening, and mechanical strength are the important points. These properties are common in many applications. The newly developed resin for each application should be designed keeping above common features.

2.2.1 PAK-01

Because the resin of PAK-01 was developed for considering wide application area, this resin satisfies the common features described above.

Table 1 shows properties of PAK-01.

<table>
<thead>
<tr>
<th>Aspect</th>
<th>Transparent and viscous liquid</th>
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<tbody>
<tr>
<td>Viscosity</td>
<td>About 60 mPa×s (25 degrees)</td>
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<tr>
<td>Exposure wavelength</td>
<td>Below 400nm</td>
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<tr>
<td>Resolution</td>
<td>20nm (observed value)</td>
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<tr>
<td>Other characteristic</td>
<td>Spin coating property</td>
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<td></td>
<td>Mold release property</td>
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Minute resin pattern down to 20nm has been already obtained by UV-NIL. Further reduction of pattern size depends on the mold fabrication in this stage. Fig. 3 shows imprint example of 100nm dot patterns on PAK-01.

Fig. 3 SEM image of 100nm dot pattern

2.2.2 Resin for dry process

From the point of view of throughput and cost, application of UV-NIL process for fabricating wafer level nanostructuring of Si is expected. Resin nanopatterns by UV-NIL can be transferred to Si substrate using succeeding dry etching, so called DEEP RIE [5]. The PAK-01 described above shows poor mask capability for Si dry etching. New resin stands up for dry etching was developed. It shows low etching rate of about half that of PAK-01, it is applicable to form high aspect ratio Si nanoholes.

Figure 4 shows the fabrication example of Si nanostructures using developed resin as an etching mask. Resin pattern sizes as the etching mask were hall diameters 250nm, and 200 nm in height. Pattern sizes of the obtained Si nanostructure were hall diameters 220nm, 1000 nm in height after it had etched, and aspect ratio 4.6 was achieved.
2.2.3 Resin for wet process

UV-NIL is also expected to nanometal structures by chemical or electrochemical wet processes of plating, etc. The chemical durability and the adhesiveness to the substrate are requested in this application. New resin, TR-11, was developed for this purpose.

Fig. 5 shows the result of durability evaluation about both PAK-01 and TR-11 to the wet process. Line and Space resin patterns of 10 μm in with, 350nm in height was made as an experiment sample. The resin was spin coated on the silicon substrate with 20mm square by film thickness 2 μm, and UV of 1000mJ/cm² was irradiated to the resin. The plating durability was evaluated referring to the electrodeposition condition in the magnetic substance pattern used in our group. Table 2 shows the experimental conditions.

The PAK-01 patterns flaked off from the substrate when it was immersed had been in the plating liquid within 20min. On the other hand, there was no change of TR-11 pattern.

PAK-01 shows better adhesion to the Si substrate than TR-11. The swelling of the PAK-01 is the problem for actual applications.

<table>
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<tr>
<th>Table 2 Experiment condition</th>
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<tr>
<td>Solution</td>
</tr>
<tr>
<td>pH</td>
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<tr>
<td>Immersion time</td>
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<tr>
<td>Drying method</td>
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3. Applications

It becomes possible to develop the various applications by using the newly developed resin. Here, the application examples of storage and LED are shown as an achievement of a joint research with the Toyo Gosei Co., Ltd.

3.1 Magnetic dot arrays

There has been much interest in the patterning of magnetic media[6][7] because of its potential to enable areal densities in magnetic recording beyond the super paramagnetic limit, where the magnetic energy stored in individual grains is too small for long-term thermal stability. Moreover, higher areal densities require smaller and smaller grain sizes for reduction of signal-to-noise ratio. Patterning the media so that bits can be written on individual magnetically isolated areas will overcome these technological issues. In this section, as an approach for the patterning the media, the fabrication example of magnetic dot arrays using UV-NIL in combination with electrodeposition is shown.

First, photocurable resin was spin-coated on a silicon substrate of 2 inches in diameter. A copper layer was formed on the surface of the silicon substrate as a seed layer for the electrodeposition of the nanopattern.

Second, a reflection of the mold’s pattern was printed on the resin with UV-NIL. UV of 1000mJ/cm² was irradiated to the resin. The actual pressure produced by the weight of about 5kgf is 0.25MPa under vacuum pressure (450hPa) while that under atmospheric pressure (1013hPa) is 0.08MPa. Imprint under vacuum removes microscopic bubbles in the resin. Figure 6 shows an SEM image of the top view of the resin pattern. The
applied pressure was 0.25 MPa under vacuum pressure at 450hPa. After imprinting, the resin has 220nm hole patterns with 500nm pitches.

Third, the residual layers were removed by O2 RIE. After etching, the size of the holes increases to 240nm and the depth is about 220nm.

Fourth, cobalt alloy was electrodeposited onto the surface of the copper seed layer. To form the Co alloy dots, a citric acid as a complex agent was added to the solution. Then pH was controlled at 6. Before electrodeposition, sulfuric acid cleaning was done as a pre-treatment. Figure 7 shows a top view SEM image of 240nm diameter Co alloy patterns. This image shows that magnetic nanodots were uniformly fabricated.

This result means that magnetic nanodot arrays can be fabricated with simple process of UV-NIL, O2-RIE and electrodeposition. Then, these processes don’t need an expensive equipment. Therefore, if this technology can be established, it can be said that this technology is effective to the mass production of the patterned media.

3.2 LEDs

Light emitting diodes (LEDs) are expected to be used as interior illumination, car lighting, and displays because of their low maintenance cost and low carrying charge. However, at present the luminescence efficiency of LEDs is small compared to that of the conventional fluorescent lamp. If the luminescence efficiency is increased, LED will be applied widely for common lighting.

High-intensity LEDs can be achieved by improving internal quantum efficiency and light-extraction efficiency. In this research, we paid special attention to light-extraction efficiency. Light-extraction efficiency leaves great room for improvement, and a large effect can be expected. Light-extraction efficiency is an important factor for higher luminescence LEDs. Light-extraction efficiency is increased by reducing the reflection of light on the surface. For this purpose, it is effective to form nanostructures on the surface of the substrate for reflection control [8]-[10].

We were able to make the metal nanoscale mask for dry etching in a large area by using UV-NIL in combination with electrodeposition; nanostructures of GaN for antireflection are fabricated by reactive ion etching (RIE) using this mask.

In conventional LEDs, the light from the active layer doesn't go out, because the majority of light reflects on the top smooth surface and is absorbed in the LED. These phenomena decrease the light-extraction efficiency.

In order to improve the light-extraction efficiency, rugged surface and photonic crystal structures formed on an LED is useful. Photonic crystal is an optical material in which the refractive index changes periodically. A photonic crystal causes light diffraction phenomena for a particular wave length. Then the photonic crystal structures formed on the surface are effective for controlling reflected light.

Figure 8 shows the cross section of an LED device that has the nanostructures fabricated in our research. Rugged patterns are periodically formed with the size at the wavelength level of light, and the effect of a photonic crystal can be expected. Nanoscale patterning is formed by UV-NIL; a metal mask for dry etching is formed by electrodeposition; and ruggedness structures are fabricated over a large area periodically.
The fabrication process consists of 5 steps as shown in Figure 9. First of all, a thin metal film that became a seed layer of electrodeposition formed on the GaN substrate surface. In addition, photocurable resin was spin-coated on the seed layer. Next, the replicated patterns were formed with the photocurable resin having resistance to electrodeposition by UV-NIL. This photocurable resin tolerates the bath liquid of the Ni electrodeposition (pH:2.8; temperature: 24 °C; immersion time: 1min). To do electrodeposition in the following process, the residual layer was removed by dry etching.

Next, Ni nanopatterns were electrodeposited to the holes using the seed layer. Ni was used as an etching mask because Ni has high resistance to Cl₂ RIE. The photocurable resin was removed after electrodeposition. Subsequently, the GaN substrate was etched by Cl₂-based inductive coupled plasma (ICP) RIE. Finally, the Ni mask and the seed layer were removed. The nanostructures of 600nm in depth, 300nm in diameter, and 500nm in pitch were formed on the surface of the GaN substrate.

Figure 10 shows the SEM image of the fabricated GaN nanostructures. The GaN substrate was etched by Cl₂-based ICP-RIE. The nanostructures are 600nm in depth. As a result, it was confirmed that the Ni film has an enough resistance for dry etching. Because the pitch of the GaN structures is equal to the luminescence wave length of LED, the effect as a photonic structure can be expected.

After forming the electrodes on the LEDs, the radiant intensity from the front surface was measured by a photodiode. A photodiode with a 78.5mm² detection area was used, and it was positioned 51.5mm from the LED.
Fig. 11 Luminous intensity of Con ventional LED and patterned nanostructures LED

Figure 11 shows the result of the radiant intensity measurement of the fabricated LED. The horizontal axis is a sample number. The vertical axis is radiant intensity mW/sr. The line shows the value of a conventional LED. Points show the values of the fabricated LEDs. The radiant intensity of the LEDs is 1.5 times larger than that of the conventional LED.

This result indicates the possibility of low-cost fabrication of nanostructures on the GaN substrate. This technology will be developed further in the future, and if utility can be confirmed by making a smaller structure, a large influence can be expected on high-intensity LEDs.

4. Conclusion

We applied UV-NIL for fabricating magnetic dot arrays and GaN structures. The NIL technology progresses rapidly for these several years a technological level, and will become practical use stage. It is considered that the NIL technology greatly contributes to industry if newly resins appropriate for many applications are developed.

5. Acknowledgement

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References