Inorganic Nano/Micropattern Fabrication Method Using Nanoimprint Lithography and Physical Rubbing

Ryota Kojima* and Takahide Mizawa

New Business Department, SOKEN Chemical & Engineering Co., Ltd.
1-13-1 Hirosehigashi, Sayama-City, Saitama 350-1320, Japan
* kojima@soken-ce.co.jp

A fabrication process was developed for inorganic nano/micropatterns, and is integrated with nanoimprint lithography using film mold, inorganic material deposition, and the removal of the deposition-layer by physical rubbing. The novel point and the most significant feature are used by not directly etching to inorganic materials but rubbing like hand-lap as physical lift-off. This combined method could be one of the promising processes to realize nano- or micro-scaled inorganic patterning more easily than conventional patterning processes in terms of production throughput, pattern resolution, and material selectivity.

Keywords: Nanoimprint, Nano/micropatterns, Inorganic materials, Deposition, rubbing

1. Introduction

In recent years, the development of nanoimprint techniques using replica film molds has become challenging in some industrial applications that require many types of devices with fine inorganic patterns. These applications include optical devices [1], dielectric nanopatterns [2], submicron-scaled magnetic material patterns [3], nano-textured glass surfaces for anti-fogging [4], structural color shifts for massive construction materials [5], and superconducting nanowire single-photon detectors [6]. The commonality of nearly all of these devices is that after processing, they are composed of only inorganic materials; because of the characteristic properties of these inorganic materials, it is extremely difficult to replace them with organic materials. In general, the use of photolithography or electron beams to draw a resist mask pattern (followed by wet- or dry-etching) is a well-known conventional process for fabricating finely patterned inorganic materials. However, this method faces industrial problems in terms of throughput, pattern area, resolution, and material selectivity. Therefore, other materials and methods are being developed to solve these problems, such as metal- nanoparticle mixtures as low-temperature firing inks for electronic wiring [7] and room

![Fig. 1. The process flow for fabrication of nano/micropatterns.](image)

- Step 1: Fabrication of film mold from replicated Ni mold.
- Step 2: Formation of resist pattern on substrate.
- Step 3: Removal of residual resist by using oxygen plasma RIE.
- Step 4: Deposition of inorganic materials.
- Step 5: Removal of pattern and planarization by rubbing.
- Step 6: Removal of resist area by using oxygen plasma RIE.
temperature sol-gel nanoimprints [8] that will allow easy fabrication of inorganic nano/micropatterns. In this study, we integrate nanoimprint lithography techniques with the deposition of inorganic materials and removal of a pattern with rubbing, which differs from conventional etching processes. The rubbing process is performed by a textile with solvent. This simple concept allows for high resolution, and the non-selectivity of materials. Thus, it opens up new opportunities in terms of trial development and industrial production. The primary feature of the integrated process is a top-down process that avoids using direct etching on inorganic materials (so that the properties are not changed). In this work, we demonstrate the process details and focus on extra-layer removal tests using textile rubbing.

2. Experimental

2.1. Fabrication of film mold

A film-mold is fabricated from a Ni mold, made with a thin layer of a patterned, UV curable resin on a PET substrate, as shown in step 1 of Fig. 1. It shows high fidelity, and the film mold allows for the fabrication of fine patterns on several types and sizes of substrates. The Ni mold used to fabricate the film mold was created by electroforming a patterned resist film from a master mold [9]. The Ni molds typically used two types of line-and-space patterns (LS-1, LS-2) and a microcavity pattern; these were used to imprint our developed UV curable resin on PET by UV-NIL, as shown in step 1 of Fig. 1. This imprinted film served as a film mold. The UV curable resin for the film mold was prepared with a photo initiator and reactive acrylate monomer, to ensure low surface energy for de-molding in the UV-NIL process. In our UV-NIL process, a nanoimprint system ST-50 (Toshiba machine Co., Ltd.) and UV exposure system (Techno vision, Inc.) were used for post-curing. The pressure and cumulative energy conditions for UV exposure were optimized.

2.2. Fabrication of resist pattern and removal of residual resin

We used a 2-inch bare sapphire substrate (Sio-American Silicon wafer Inc.) for inorganic nano/micro patterns. First, the surface of the sapphire substrate was activated with reactive ion etching (RIE) (PC300, SAMCO Inc.) using oxygen gas to uniformly coat the UV curable resist without de-wetting. Then, the UV curable resist was spin-coated such that the thickness of the residual resist was less than 100 nm (1H-DX2, Mikasa Co., Ltd.). The resist thickness was calculated from the volume of fine patterns confirmed by a non-contact optical thickness measurement system, F20 (Filmetrics Inc.). Next, the resist was imprinted using a nanoimprint instrument (ST-50, Toshiba machine Co., Ltd.), with a film-mold as shown in step 2 of Fig. 1. The pressure, degree of vacuum, and cumulative energy of UV exposure, were 3 MPa (30 s), 1000 Pa, and 1000 mJ/cm², respectively. The UV light was used under vacuum. Then, the patterned resist on the sapphire substrate was manually demolded from the film mold. Residual resist existed between the clearances of the pattern. Finally, in an effort to anchor inorganic material to the substrate, the residual resist was removed by RIE, as shown in step 3 of Fig 1. The RIE conditions of oxygen flow, output, and time were 10 scm, 250 W, and 30 s, respectively. In a series of processes, the patterned resist without the residual resist was obtained.

2.3. Deposition of inorganic materials

For the deposition of inorganic materials, a magnetron sputter (Hitachi Zosen Corporation) with a Ni target was used for deposition, as shown in step 4. A Ni layer was formed, ranging from 20 nm to 400 nm. The LS-1 pattern was used as a Ni coverage test. The argon flow, degree of vacuum, and electrode output were 60 scm, 0.5 Pa, and 5 A, respectively. The thickness of the sputtered Ni was measured by F20. SiO₂ was layered by physical vapor deposition at 40 nm as the other material.

2.4. Pattern removal and planarization

In the process shown in step 5 in Fig. 1, the rubbing likes hand-lap used to remove the resist pattern was a textile saturated primarily with ethyl acetate (an organic solvent). The LS-2 and microcavity pattern were used as removal tests to determine whether an anti-sticking reagent (HD-2100, Daikin) was required. When the anti-sticking reagent was used, a sample that had already been rubbed was dipped in the reagent at room temperature for 1 h. Some debris (the pattern destroyed by rubbing) remained and adhered onto the pattern surface, including the clearance of pattern cavities. After 1 h, the dipped sample was rinsed with a perfluorocarbon solvent (NOVEC 7500, 3 M). Next, the textile was saturated with ethyl acetate in adequate amount. Then, the sample surface was rubbed with the wet-textile likes hand-lap, which was exchanged with a new one unless almost no debris remained. Without debris, the
perfluorocarbon solvent was saturated into the textile and the sample surface was wiped. Finally, the surface of the sample was treated with RIE as described to remove the residual resist, as shown in step 6 of Fig. 1.

2.5. Measurement of pattern profiles

Pattern profiles were measured using images from a scanning electron microscope (S-4800, Hitachi High-tech. Science Corp.) and scanning probe microscope (SPM, Hitachi High-Technologies Corporation) as presented in Table 1. The measurement area was the center of the sample and the value was averaged from five measured points in the patterns. In order to confirm the cross-section images, the sapphire substrate was cut with a glasscutter and then observed. For microscale observation, we used optical microscopy (OM) (ECLIPSE N300L, NIKON Corporation). Additionally, we used a digital camera to confirm visual differences before and after rubbing.

3. Results and discussion

3.1. Fabrication of film mold

The measurement values for the two LS patterns (LS-1, LS-2) and micro-cavity pattern from Ni mold to film mold are presented in Table 1, which includes descriptions of the surface images. The calculated transcription values in percentage terms were higher than 95% for all profiles, indicating high transcriptional precision. The height of each pattern decreased by up to approximately 5% for LS-2 and the micro-cavity pattern, because UV curable resin shrinks when curing because of the reactions of the monomers. With respect to film mold durability, the surface of the cured resin had low surface energy, so that the film mold would be usable for imprinting as the stamper, without requiring an anti-sticking reagent for mold release [10].

3.2. Fabrication of patterned resist

The patterned resists for LS-1, LS-2, and the micro-cavity that were imprinted from film molds were measured, as presented in Table 1. In addition to the fabrication of the film mold as described above, the height of each pattern was decreased. It was thought of shrink of the resist. As lower nanoimprint process, there was more decrease of the height of pattern. These patterned resists were treated by RIE to remove the residual resist, as described in step 6 of Fig. 1. The finishing point of residue resist removal occurred when the pattern height was increasingly lowered by RIE. These points were confirmed using SPM. We can approximate the RIE processing time, because the thickness of the residual resist was fixed at less than 100 nm and the RIE etching rate of the resist was 50 nm per minute.

Fig. 2. Confirmation of visual differences before and after rubbing the micropillar pattern. (a) overall digital picture. The 30 mm × 30 mm area in the center is the pattern area. The diluted color area at the top-right is the post-rubbing state. The dark area (excluding the top-right in the pattern area) is the pre-rubbing state area. The inserted image illustrates the state before and after rubbing. (b) and (c) are OM images of the border before and after rubbing in the same area. (b) is focused on after rubbing. (c) is focused on before rubbing.

Table 1. The profile of each pattern at the replicated Ni mold, film mold, and the imprinted resist.

| Pattern images | LS-1 | LS-2 | Cavity (Reverse pattern : pillar) |
|----------------|------|------|----------------------------------|
| Replicated Ni mold | P : 1005 nm  W : 635 nm  H : 742 nm | P : 2000 nm  W : 1276 nm  H : 986 nm | P : 2947 nm  D : 1686 nm  H : 1713 nm |
| Film-mold | P : 1006 nm  W : 420 nm *  H : 736 nm | P : 2000 nm  W : 754 nm ***  H : 946 nm | P : 2993 nm ****  D : 1735 nm ****  H : 1710 nm **** |
| Imprinted resist | P : 1001 nm  W : 632 nm  H : 730 nm | P : 2000 nm  W : 1270 nm  H : 943 nm | P : 2954 nm  D : 1675 nm  H : 1642 nm |

* SEM images were used for measurement of period, diameter, and width of pattern profile.
** SPM images were used for measurement of height of pattern profile.
*** Line pattern was reversed to space pattern  **** Micro-cavity pattern due to reverse pattern of micro-pillar pattern
Therefore, processing occurred within a few minutes, and the processed sample was used as a template for inorganic nano/micropatterns.

3.3. Deposition of Ni

The patterned resist (with residual resist removed by RIE) was treated with 400 nm of Ni depositions. The Ni layer was confirmed by its metallic color and by the F20 measurement of the non-patterned area. LS-1 was believed to be commonly affected by the deposition coverage because its pattern was smaller and narrower than the others. Additionally, the different heights of the LS-1 pattern, which we selected as having a significant influence, were prepared by RIE over-treatment. With the higher height of the LS-1 pattern, a worse coverage area was observed by cross-section SEM images, and the quantity of deposition materials in the clearance of the pattern decreased. Its shape became a triangle, as shown in Table 2. In actuality, the thicknesses of the Ni deposition onto the pattern clearance changed from 331 to 384 nm. This phenomenon is known as shadowing, and occurs when the patterned resist prevents the invasion of Ni vapor into the pattern clearance. This problem can be overcome by the use of a mask or a change in the deposition rate that cancels the oblique incidence of vapor materials. Alternatively, we can use unconventional deposition techniques such as atomic layered deposition (ALD). Consequently, it is difficult for a physical rubbing method to fabricate a high aspect pattern made from inorganic materials and a uniformly rectangular geometric pattern, unless the shadowing problem can be solved.

3.4. Rubbing a patterned surface

Patterned surfaces with either LS-2 or micro-cavity patterns were fabricated by rubbing as previously described. We confirmed that the line-edge-roughness (LER) of the LS-2 pattern increased with the thickness of the deposition (data not shown). It is thought of as destroying the continuous Ni layer, so that good coverage triggers bad roughness. To suppress roughness, we considered using not physical textile rubbing but chemical mechanical polishing (CMP). Additionally, we experimented with the effect the deposition thickness had on the possibility of using the rubbing method to remove the LS-2, micro-cavity, and pillar patterns. The hardness results when rubbing to remove the pattern are presented as an organoleptic examination in Table 3. From Table 3, the number of asterisks indicates the rubbing hardness necessary to remove the pattern. Thus, it is the degree of difficulty involved in changing the color, as shown in Fig. 2 (a). The pattern was not easy to destroy, because the cavity pattern in Table 3 did not have a prominent pattern and had a large contact area between the resist and substrate. In contrast, the other patterns in Table 3 (which had prominent

Table 2. Ni coverage experiment with LS-1 pattern

| SEM image | Height of Ni in pattern clearance (Yellow arrow*) | Height of resist pattern (Red arrow**) | Ni shape |
|-----------|-----------------------------------------------|-------------------------------------|----------|
|           |                                               | 331 nm                              | Triangle |
|           |                                               | 371 nm                              | Trapezoid |
|           |                                               | 384 nm                              | Trapezoid |

*Yellow dashed curve line: the surface of Ni between the clearances of resist pattern. **Red dashed line: the border of the resist and Ni.

2.5 nm per second. Therefore, processing occurred within a few minutes, and the processed sample was used as a template for inorganic nano/micropatterns.

Table 3. Hardness for rubbing each pattern

| Resist pattern  | LS-2 | Micro-cavity | Micro-pillar |
|-----------------|------|--------------|--------------|
| Ni thickness    |      |              |              |
| 20 nm           | ***  | **           | ***          |
| 100 nm          | ***  | *            | ***          |
| 200 nm          | **   | *            | **           |

*** : 1 pass rubbing with slight pressure  ** : 1 pass rubbing with shoving  * : multi-pass rubbing with shoving

Fig. 3. SEM images of the surface of Ni LS-2 pattern after rubbing and the difference in debris removal with and without the anti-sticking reagent. (a) Using anti-sticking reagent. (b) Not using anti-sticking reagent.
resist patterns) were easily fabricated by rubbing. In addition, the debris resulting from the destroyed pattern after rubbing remained on the overall surface and on the pattern clearances. Therefore, it is important to test the debris removal efficiency. The removal of debris was tested as shown in Fig. 3. The debris on the sample was treated by an anti-sticking reagent as a paddle before rubbing. The adhesion of the debris was considered to be suppressed because of the anti-sticking reagent attached to the Ni surface, which was easily rinsed by perfluorocarbon solvent. Additionally, the debris, which comprised uniformly sized pattern micro-rods broken off from the root, was observed by optical microscope as shown in Fig. 4. The micro-rod has high dispersion stability in the perfluorocarbon solvent. In terms of the submicron-scale, the submicron-rod, which has a period of 240 nm, was fabricated by rubbing using the same method as described above. We confirmed that these conditions could be applied for other inorganic materials, such as SiO$_2$, Al$_2$O$_3$, ZrO$_2$, and Cu/Cr with various thickness. Finally, a multi-layered submicron-dot composed of SiO$_2$ and Ni as a dielectric and conductive material was fabricated from a resist pattern with a micro-cavity pattern, as shown in Fig. 5. The dot-pattern was composed of three layers of 40 nm SiO$_2$ and 20 nm Ni. We confirmed that the multiple inorganic material layers were fabricated by these methods.

4. Conclusion

We demonstrated that it was possible to fabricate a finely patterned inorganic material by integrating nanoimprinting, inorganic material deposition, and extra-layer removal by rubbing likes hand-lap. However, there was a limit for the thickness of the inorganic materials, which influenced the LER and determining whether it was possible to fabricate finely patterned inorganic materials. On the other hand, this process allowed for greater latitude in the selection of inorganic material types. To improve the accuracy of the LER and realize a higher aspect ratio of the pattern, we think that the process could be combined with high-coverage inorganic material methods such as ALD and CMP.

References

1. T. Dietrich, S. Piehler, M. Rumpel, P. Villeval, D. Lupinski, M. A. Ahmed, and T. Graf, Opt. Express, 25 (2017) 4917.
2. K. Xu, D. Chen, F. Yang, Z. Wang, L. Yin, F. Wang, R. Cheng, K. Liu, J. Xiong, Q. Liu, and J. He, Nano Lett., 17 (2017) 1065.
3. A. Kikitsu, J. Magn. Magn. Mater., 321 (2009) 526.
4. K. C. Park, H. J. Choi, C. H. Chang, R. E. Cohen, G. H. McKinley, and G. Barbastathis, ACS Nano, 6 (2012) 3789.
5. H. Fudouzi, Nanomaterials and Nanoarchitectures, Chapter 1 (2015) 1-19.
6. T. Yamashita, S. Miki, H. Terai, and Z. Wang, Opt. Express, 25 (2017) 5832.
7. X. Y. Zhang, J. J. Xu, J. Y. Wu, F. Shan, X. D. Ma, Y. Z. Chen, and T. Zhang, RSC Adv., 7 (2017) 8.
8. T. Kaneda, D. Hirose, T. Miyasako, P. T. Tue, Y. Murakami, S. Kohara, J. Li, T. Mitani, E. Tokumitsu, and T. Shimoda, J. Mater. Chem. C, 2 (2014) 40.
9. R. Kojima and T. Mizawa, J. Photopolym. Sci. Technol., 26 (2013) 105.
10. R. Kojima, Y. Mizukami, and T. Mizawa, The 12th Internarional Coference on Nanoimprint and Nanoprint Technology (2013).