Fabrication of Complex 3D Nanoimprint Mold by Using Acceleration Voltage Electron Beam Lithography

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In this study, we focused on the fabrication of biomimetic structures using nanoimprint lithography (NIL). Biomimetic structures are an attractive approach to create functional products. Among the various biomimetic structures, we focused on rose petals for superhydrophobicity characteristics with high contact angles and the surface properties of the water droplets and shark skin for the reduction of fluid resistance. These bio-inspired molds were fabricated by electron beam lithography (EBL). Many of the biomimetic structures are micro- and nano-sized 3D structures; rose petals and shark skin also have fine-grained 3D structures. Dose modulated EBL is commonly used for the fabrication of 3D structures. On the other hand, our previous study revealed that precise depth control is possible by changing the acceleration voltage. Therefore, the 3D nanoimprint mold was fabricated using a combination of conventional dose modulated and acceleration voltage modulated EBL. As a result, bio-inspired 3D molds (rose petals and shark skin) were obtained. The depths of these molds could be controlled by the characteristics of the electron penetration depth. Using these molds, convex biomimetic structures were obtained by UV-NIL. In this study, the fabricated structures had steps. We believe that a smooth shape can be fabricated by using a various acceleration voltage. And we believe that this process, using acceleration voltage modulation EBL, can fabricate precise and complex nano-scale 3D mold structures.

Keywords: Nanoimprint mold, Electron beam lithography, Three-dimensional structure, Acceleration voltage modulation

1. Introduction

Biomimetic structures are an attractive approach to create functional products. For example, the moth-eye structure used for an antireflection effect [1] and shark skin used for reduction of fluid resistance [2-4] are well-known biomimetic structures, which have three-dimensional structures on the nano-scale. To produce these structures, nanoimprint lithography (NIL) [5-7] is used because it is a powerful tool for fabricating the production of fine patterns with high-throughput. Thus, the fabrication method of biomimetic structured NIL mold is important. One method of fabrication of the NIL mold is electron beam lithography (EBL). Generally, the dose modulation method is used when fabricating a three-dimensional structure with EBL. On the other hand, our previous study revealed that precise depth control is possible by changing the acceleration voltage [8-10]. It is easy to control developing depth with acceleration modulation of the EBL because the penetration depth of the electrons is limited. Therefore, we focused on the fabrication of a biomimetic structure mold using the accelerated voltage modulation method. In this study, the biomimetic structures being investigated are the rose petal and the shark skin structures. These are well-known in the field of biomimetic structures.

Some rose petals have superhydrophobicity with high contact angles [11]. Unlike the characteristics of the lotus leaf, water droplets stay pinned to the
surfaces of the petals. This phenomenon has been reported as the petal effect [12]. The phenomenon has the potential for applications such as the controlled transport of small volumes of liquid and single molecule spectroscopy [13,14]. The surface of the petal of rose has microstructures, such as mountains, and the microstructures themselves have nanofolds [15]. There are several ways to fabricate an artificial rose petal; however, none of these methods used electron beam lithography. Therefore, we present an artificial rose petal composed of micro- and nanostructures using acceleration voltage modulation.

In addition to the rose petal, we studied the structure of shark skin for the reduction of fluid resistance. Kirchner et al. have reported a method for the generation of 3D surfaces based on the melting process of developed EB resin [16,17]. Furthermore, they reported bio-inspired 3D funnel structures using EBL and the melting process [18]. This method can be used to create smooth 3D surfaces with nano-scale resolution. The feature of the biomimetic structure has a deep narrow space and a shallow but gradually changed space in the order of micron. We present a fabrication method for the shark skin using acceleration voltage modulation without the EB resin melting process. Unlike the fabrication process of the rose petal, the dose modulation method is also used for the shark skin. Our strategy for the fabrication of such structure is as follows: the deep narrow structure is exposed by high acceleration voltage EBL, and the shallow, gradually changed space is exposed by low acceleration voltage with the dose modulation method. The target structure is a 3D funnel structure to confirm the performance of our method. Fabricated 3D molds have a concave pattern. Finally, we obtained the replica pattern by UV-NIL [19,20] using fabricated molds.

2. Experimental methods and materials

2.1. Investigation of positive-tone organic electron beam resist, SML2000

Figure 1 shows the overview of the experimental method. First, SML2000 (EM RESIT Ltd.) was spin coated onto the Si substrate. This resist is a positive tone organic resist that has been produced to have similar processing parameters to poly methyl methacrylate (PMMA), but with enhanced performance [21]. Soft bake was carried out on the hotplate at 80 °C for 5 min. Hard bake was cured in the electric furnace at 180 °C for 20 min. This yielded a 3000-nm thick resist layer.

Next, the sample was irradiated by the electron beam. ERA8800-FE (ELIONIX Co.) was used as the EB system with 50 pA of beam current. Then, EB acceleration voltage was set between 2.5 kV to 15 kV. The electron beam lithography design pattern consisted of 20 μm by 900 μm rectangles. The exposure dose ranged from 5 to 200 μC/cm². The exposed sample was developed by ZED-N50 (Zeon Co.) for 60 s. Measurements of the pattern depth were carried with the step profilometer (Alpha-Step500, KLA_Tencor Co.).

2.2. Fabrication of a rose surface inspired 3D structure

The EBL design pattern is shown in Fig. 2. First, the circle pattern was drawn at 7.5 kV, 10 kV, and 12 kV. This pattern’s pitch was approximately 14 μm. Then, the applied EB doses were 50 μC/cm² at 7.5 kV, 100 μC/cm² at 10 kV, and 120 μC/cm² at 12 kV. The design value of the dot size was 90 nm on a pitch of 450 nm, and the EB dose was 180 μC/cm².

Figure 3 shows the experimental method. The exposed areas of the SML2000 film were etched away by treatment with the ZED-N50 solution for 60 s, followed by an IPA rinse and blow dry. After developing, the sample was baked at 80 °C for 5 min and exposed once more. The dot pattern was drawn on areas that had already been developed. Similarly, the exposed areas of the SML2000 film were etched away by treatment with the ZED-N50 solution for 60 s, followed by an IPA rinse and blow dry. Next, approximately 30 nm of the chromium layer was deposited on the fabricated 3D mold by vacuum evaporation (VPC-260F,
Ulvac Kiko Inc.). The mold was coated with a release agent of optool DSX 1% (Daikin Industries Ltd.). A replica pattern of the mold was fabricated by the UV-NIL process using UV curable resin (PAK-01 CL, Toyo Gosei Co., Ltd.) on polyester film (Cosmoshine A4300, Toyobo Co., Ltd.). A replica pattern was fabricated using parallel plate UV-NIL. The UV-NIL pressure was 3.0 MPa, the exposure time was 30 s, and the UV dose was 2.4 J/cm².

Fig. 2. Model diagram of the 3D structure / EBL design pattern.

2.3. Fabrication of a shark skin inspired 3D structure

EBL design pattern is shown in Fig. 4. The three-dimensional structure in the x-axis was exposed with acceleration voltage modulation. The acceleration voltage was set at 5 kV, 7.5 kV, and 10 kV. The shallow spaces were exposed by 5 kV and 7.5 kV acceleration voltages. In addition, gradually changed area depths were controlled by EB dose modulation. In this case, the EB dose exposed at the center of the pattern was 60 μC/cm², which later reduced to 39 μC/cm², and finally reached 37 μC/cm² when moved outside (y-direction) at 7.5 kV. Similarly, pattern depths at 5 kV can be presumed to be 377 nm, 307 nm, and 260 nm from the center of the pattern. The EB dose at 10 kV was 120 μC/cm². The pattern depth at 10 kV was estimated to be 1633 nm.

Fig. 4. (a) Model diagram of the 3D mold; (b) The EBL design pattern; (c) Control depth of the two processes.

The experimental method is shown in Fig. 5. The EB exposed areas of the SML2000 film were etched away by treatment with the ZED-N50 solution for 60 s, followed by an IPA rinse and blow dry. Next, approximately 30 nm of the chromium layer was deposited on the fabricated 3D mold by vacuum evaporation. The mold was coated with a release agent of optool DSX 1%. A replica pattern of the mold was fabricated by the UV-NIL process using UV curable resin on polyester film. As with the experimental method in Section 2.2, a replica mold was fabricated using parallel plate UV-NIL. The UV-NIL pressure was 1.5 MPa, the exposure time was 30 s, and the UV dose was 2.4 J/cm². The mold and replica pattern were observed with an atomic force microscope (SPM-9600, Shimadzu Co.).

Fig. 5. Fabrication method and replica pattern of the shark skin mold.
3. Results and discussion

3.1. Investigation of positive-tone electron beam resist, SML2000

Figure 6 shows the developed depth from the resist surface against EB doses.

As seen in Fig. 6, exposure less than 10 kV cannot be cleared, and the remaining resist thickness saturates. It shows that the penetration depth of the electrons is limited and decreases with decreasing acceleration voltage. On the other hand, penetration depth of the electrons at 15 kV reaches Si substrate. By using saturation region, we can easily control the developing depth and fabricate 3D structures.

3.2. Fabrication of a rose surface inspired 3D structure

Figure 7 shows the rose surface inspired mold fabricated using acceleration modulation electron beam lithography. The pattern depths are approximately 0.8 μm at 7.5 kV and 2.0 μm at 12 kV. This demonstrates that the depths at 7.5 kV and 12 kV are similar to the characteristics of the developing depth. 10 kV pattern was inclined from the influence of 7.5 kV and 12 kV pattern. The diameter of the dot pattern is approximately 172 nm. The diameter of the circle pattern is approximately 6.9 μm.

3.3. Fabrication of a shark skin inspired 3D structure

Figure 9 shows the shark skin inspired mold fabricated using the acceleration and dose modulation electron beam lithography. We fabricated the shark skin inspired 3D mold, but the pattern position is slightly misaligned. This can be attributed to using stepping motors on the SEM stage. These motors have a limited accuracy of approximately 500 nm. Table 1 shows the developing depth of the design value and the fabricated mold using acceleration modulation. Table 2 shows the developing depth of the design value and the fabricated mold using dose modulation at 5 kV and 7.5 kV.
Table 1. Developing depth of the design value and the fabricated mold by acceleration modulation.

| Acceleration | 5 kV | 7.5 kV | 10 kV |
|--------------|------|--------|-------|
| Design value [nm] | 377 | 834 | 1633 |
| Measured value [nm] | 452 | 922 | 1607 |
| Error [%] | +19.9 | +10.6 | -1.59 |

Table 2. Developing depth of the design value and the fabricated mold using dose modulation at 5 kV and 7.5 kV.

| Dose [μC/cm²] | Low | Middle | High |
|---------------|-----|--------|------|
| 7.5 kV | Design value [nm] | 420 | 510 | 834 |
| | Measured value [nm] | 613 | 780 | 922 |
| 5 kV | Design value [nm] | 260 | 307 | 377 |
| | Measured value [nm] | 342 | 392 | 452 |

The results show a trend in that each developing depth is deeper than the design value because irradiated electrons are scattered within the resist, which influenced the fabrication between neighboring patterns. The developed pattern size is larger than the design value, which is also due to irradiated electrons are scattered within the resist. This effect is termed the “proximity effect” in EBL [22,23].

Figure 10 shows the replica pattern by using the fabricated mold, and Table 3 shows the developing depth of the fabricated mold and the height of the UV-NIL pattern.

The results show that each height of the UV-NIL pattern tends to be shallower than the developing depth because the UV curable resin shrank due to UV irradiation [24-26]. The mold of the 10-kV pattern was shallower than the design value because the cantilever of the AFM could not reach the pattern bottom. Therefore, the mold of the 10-kV pattern was shallower than the mold of the replicated pattern.

4. Conclusion

We examined the developing depth of the SML2000 with changing acceleration voltages. The characteristics of the developing depth were investigated in this study. We fabricated bio-inspired 3D molds because it is possible to control the developing depth using the characteristics. As a result, we successfully fabricated the rose petal inspired mold by acceleration voltage modulation EBL. Additionally, the shark skin mold was fabricated by combining the conventional fabrication 3D structure method, the dose modulation, and the acceleration voltage modulated EBL. The depths of these molds were similar to the characteristics of the electron penetration depths. The results show that it is possible to accurately control 3D shapes by acceleration voltage modulation EBL. In this study, the fabricated structures had steps. We also established that a smooth shape can be fabricated using a various acceleration voltage. In addition, the replicated pattern was obtained by UV-NIL using these 3D molds. The obtained replica patterns have 3D structures similar to those of

Table 3. Developing depth of the fabricated mold and the height of the UV-NIL pattern.

| Acceleration voltage | 10 kV | 7.5 kV | 5 kV |
|---------------------|-------|--------|------|
| Dose [μC/cm²] | 120 | 37 | 39 | 60 |
| Mold [nm] | 1607 | 613 | 780 | 922 |
| Replica [nm] | 1670 | 550 | 785 | 889 |
| Error [%] | +3.92 | -10.3 | -2.82 | -3.58 |

Fig. 10. SEM image of the resulting replica pattern by UV-NIL (Left: Top view, Right: Tilted view (75°)).
fabricated molds. Thus, it was shown that various complex 3D structures can be fabricated using acceleration voltage modulated EBL as well as UV-NIL.

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