Review Article

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Fabrication of bio-inspired 3D nanoimprint mold using acceleration-voltage-modulation electron-beam lithography

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Abstract: Methods for fabricating micro- and nanoscale three-dimensional (3D) structures such as electron-beam lithography (EBL) attracted attention in various fields. In EBL, an acceleration-voltage modulation method can be used to control the developing depth of the structure. In this study, we fabricated a rose petal structure using acceleration-voltage modulation. Using a rose petal mold, plastic- and silver-duplicated rose petals were prepared using nano-imprint lithography (NIL). We demonstrated that various complex 3D structures and materials can be duplicated using NIL by applying an acceleration-voltage modulation method.

Keywords: acceleration-voltage modulation; electron beam lithography; nanoimprint mold; three-dimensional structure.

1 Introduction

Recently, various methods for fabricating micro- and nanoscale three-dimensional (3D) structures have attracted attention for applications such as microelectromechanical systems (MEMS) and superhydrophobicity structures [1–6]. Electron beam lithography (EBL) is considered a powerful tool for the fabrication of such structures because the beam diameter is focused at a few nanometers. The dose-modulation method is a commonly used 3D processing method for EBL. This method is used to control the developing depth by changing the injection amount of electrons. In contrast, an acceleration-voltage modulation method can be used to control the developing depth by changing the acceleration voltage, as demonstrated in our previous study. If the acceleration voltage is used in regions where only forward scattering occurs, the penetration depth of electrons becomes the developing depth, and control of the developing depth becomes easy. In addition, the merit of acceleration-voltage modulation is that depth can be controlled by acceleration and line width can be controlled by the dose. As dose modulation changes both the depth and line width, the line width increases for the development of a deep pattern. In general, for EBL, it is impossible to focus the electron beam finely at a low acceleration voltage, and thus, there is a tendency to use a high acceleration voltage. However, in a previous study, we succeeded in obtaining a pattern of less than 100 nm using a low acceleration voltage of 1 kV [7]. In addition, we successfully fabricated a staircase-like 3D structure by combining patterns obtained using seven different acceleration voltages [8]. In addition, as the depth of penetration of electrons becomes the depth after development, the depth can be easily controlled even with a resist of high contrast. A low-acceleration-voltage EBL system is desirable because of its higher sensitivity and because it uses less costly equipment. In this study, we attempted to apply an acceleration-voltage modulation method to fabricate a more complex biomimetic structure.

Biomimetics is an attractive approach used in various fields to create functional structures. Well-known biomimetic structure examples include lotus leaves and rose petals with superhydrophobicity [9–11]; shark skin, snake skins, and sandfishes that can reduce friction [12–14]; and a moth-eye structure with an antireflection effect [15]. In this study, we focused on creating fine rose petal-inspired 3D structures and attempted to fabricate the structures using an acceleration-voltage modulation method.

Some rose petals have nanoscale protrusions with microscale-mountain-like shapes and exhibit superhydrophobicity. Unlike lotus leaves, there is a phenomenon

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in which dropped water droplets remain on the surface of a rose petal, which is called the petal effect [16]. There have been several fabrication examples of an artificial rose petal structure, although none were made using EBL.

Nano imprint lithography (NIL) is another extremely powerful method for fabricating fine patterns [17–19]. NIL attracted attention because it can be used to produce nanopatterns with high throughput, high resolution, and low cost. Using NIL, it is possible to duplicate various materials by selecting an appropriate transfer resin. If a metal ink is used as the transfer resin, it is also possible to fabricate a metal pattern. In this study, we fabricated a concave 3D biomimetic mold, which was used for NIL through EBL and transcribed using the mold. For the NIL material, not only plastic but also silver ink was used for the transfer, and the metal pattern was duplicated.

2 Experiment

2.1 Preliminary investigation of positive-type electron-beam resists

Two positive-type electron-beam resists, CSAR62 (ALL RESIST Ltd., Germany) and SML2000 (EM RESIST Ltd., UK), were used in this study. SML2000 has similar processing parameters as polymethylmethacrylate (PMMA) but with enhanced performance [20]. We investigated the effect on the resist on controlling the developing depth using acceleration-voltage modulation. For CSAR62, the resist was spin coated onto a 1-cm^2 Si substrate at 10 000 rpm for 60 s. A hard bake was applied using an electric furnace at 150°C for 30 min, and a resist thickness of approximately 370 nm was obtained. For SML2000, the resist was spin coated onto a 1-cm^2 Si substrate at 1500 rpm for 60 s. A hard bake was applied using an electric furnace at 180°C for 20 min, and a resist thickness of approximately 3000 nm was obtained. Next, the sample was exposed to an electron beam by changing the acceleration voltage. We used an ERA8800-FE (ELIONIX Co., Japan) as the electron-beam system. The EBL design pattern was made up of 20 μm×900 μm rectangles. The exposed sample was developed for 60 s using a ZED-N50 (Zeon Co., Japan). Finally, we measured the pattern depth using a step profilometer (Alpha-Step, KLA Tencor Co., USA).

Figure 1 shows the relationship between the developing depth of CSAR62 from the resist surface and the EB dose.

With exposure at 3 kV or less, the developing depth did not reach the substrate, and the resist film remained. This result indicates that the penetration depth of electrons was limited by a decrease in energy, and the developing depth was decreased at a lower acceleration voltage. Above 4 kV, the electrons reached the Si substrate. For a thin-film resist, it is difficult to control the depth using the dose-modulation method because the developing depth changes greatly with a low-dose amount. However, if a region in which the developing depth of the low acceleration voltage is

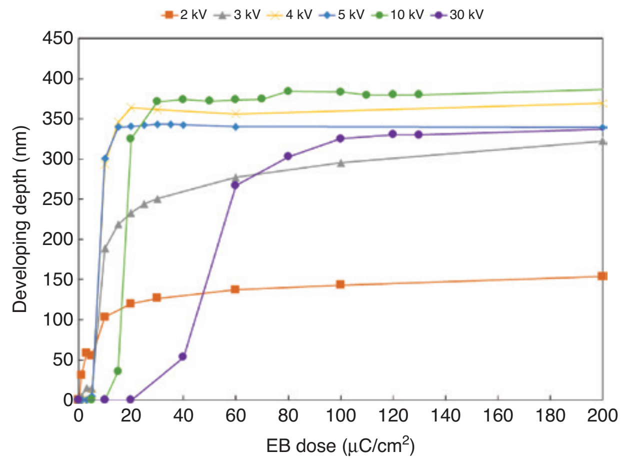

Figure 1: Developing depth of CSAR62 as a function of acceleration voltage.

saturated is used, control of the developing depth becomes easy even with a thin film.

Figure 2 shows the relationship between the developing depth of SML2000 from the resist surface and the EB dose.

With an exposure of 10 kV or less, the developing depth did not reach the substrate, and the resist film remained. This result indicates that the penetration depth of electrons was limited by a decrease in energy, and the developing depth decreased at a lower acceleration voltage. At 15 and 20 kV, the electrons reached the Si substrate. Using a dose in the range in which the change in depth is saturated, the developing depth becomes easy to control. With increasing acceleration voltage, the dose required to reach the saturation region at the developing depth increases. On increasing the accelerating voltage of irradiated electrons, i.e. on increasing the energy of electrons, the energy absorbed in the resist is reduced. In other words, the effect on the resist is weakened, and the sensitivity

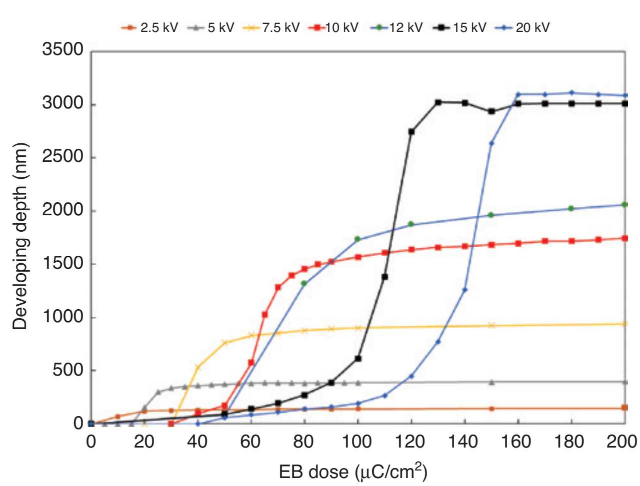

Figure 2: Developing depth of SML2000 as function of acceleration voltage.

is reduced [21]. In subsequent experiments, this resist was used to fabricate a higher 3D structure.

2.2 Fabrication of 3D micro-nano hybrid structure using acceleration-voltage modulation

We investigated the conditions under which the nanoscale dot pattern could be fabricated onto the micropattern using an acceleration-voltage modulation method. Figure 3 presents a schematic illustration of the experimental method. On the basis of the results in Section 2.1, we used SML2000 to obtain a thick film to allow for easy fabrication of the 3D structure. The micro pattern was exposed at 7.5 kV, the EB dose was 100 μC/cm², the nano dot pattern was exposed at 20 kV, and the EB dose was 180 μC/cm². In this experiment, two types of processes were investigated: (A) exposure of the micropattern lines followed by exposure of the nano dots and finally simultaneous development and (B) exposure and developing of micro line patterns followed by exposure and development of nano dots. Figure 4 shows the EBL design pattern. For process (A), the pitch and diameter of the dot pattern were 720 and 180 nm, respectively. For process (B), the pitch and diameter of the dot pattern were 540 and 90 nm, respectively. To confirm clearly

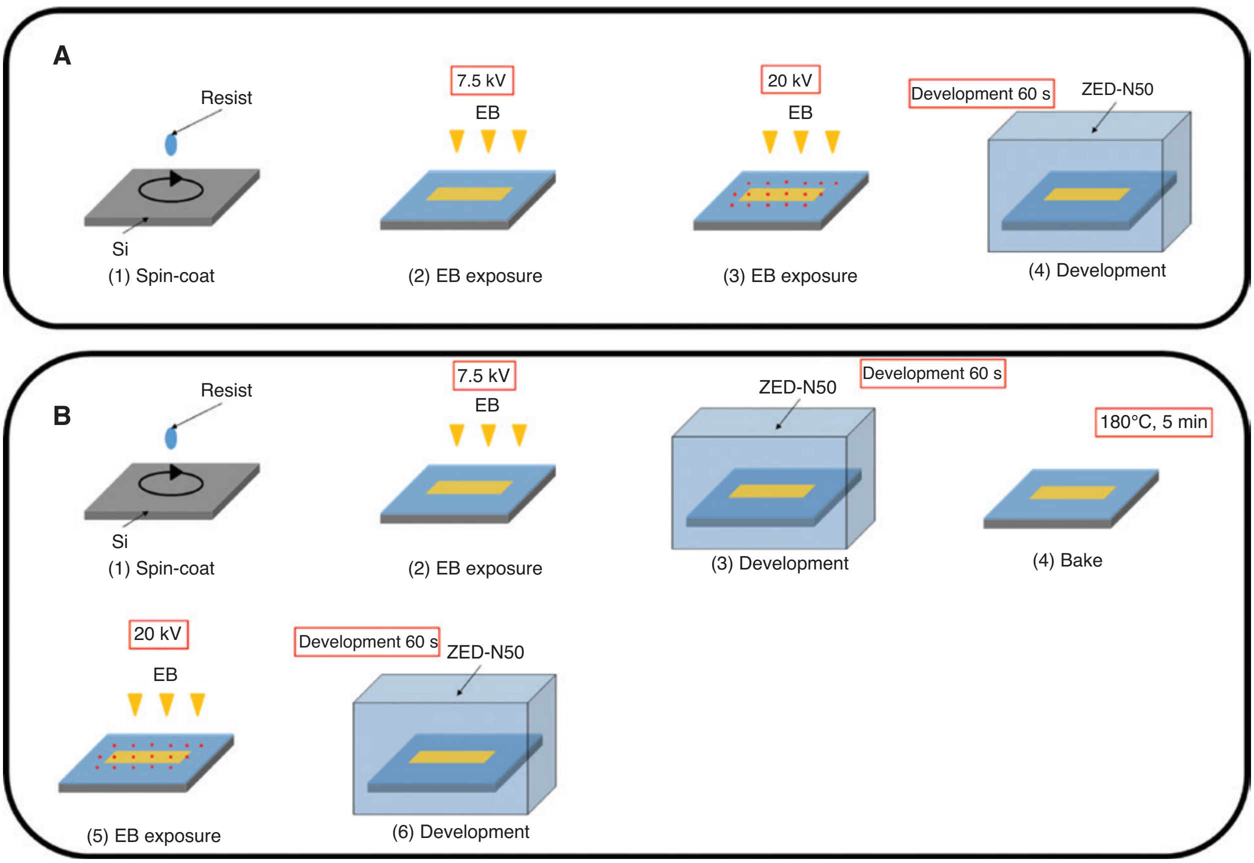

Figure 3: Fabrication of 3D micro-nano hybrid structure: (A) development processing once and (B) development processing twice.

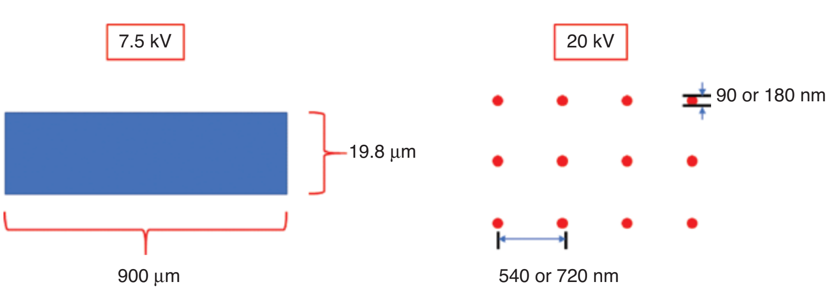

Figure 4: EBL design pattern.

after developing the dot patterns, therefore, the diameter of the dot pattern in (A) was set at 180 nm. On the other hand, the diameter of the dot pattern in (B) is a required value of the petal structure, and is set at 90 nm, which is smaller than that in (A).

The fabricated 3D micro-nano hybrid structure is shown in Figure 5.

When simultaneously exposing the resist to acceleration voltages of 7.5 and 20 kV, it was impossible to fabricate a dot pattern on the micro pattern. According to the results in Section 2.1, the penetration depth of electrons was sufficiently different. Figure 6 shows a cross-sectional view of only the micro pattern, and Figure 7 shows a cross-sectional view of pattern (A).

The depth of only the micro pattern was approximately 960 nm, which is nearly the same as that of the characteristic of developing depth of SML2000. However, when a nano dot pattern was drawn on the micropattern, the dot pattern did not appear, but the pattern

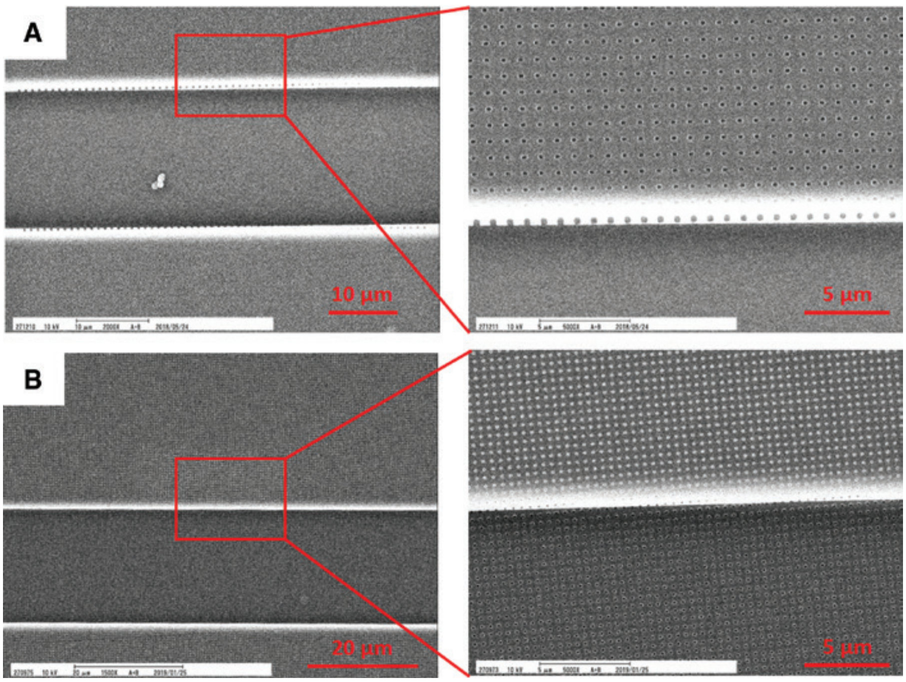

Figure 5: Fabricated 3D micro-nano hybrid structure: (A) development processing once and (B) development processing twice.

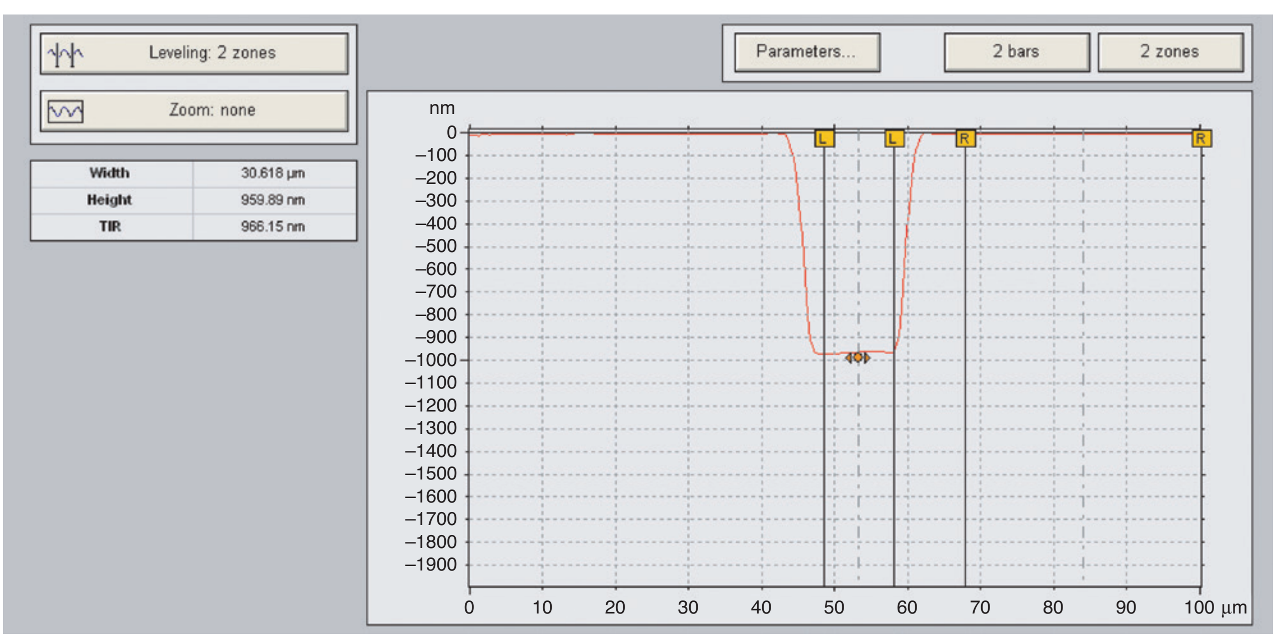

Figure 6: Cross-sectional view of only the micro pattern.

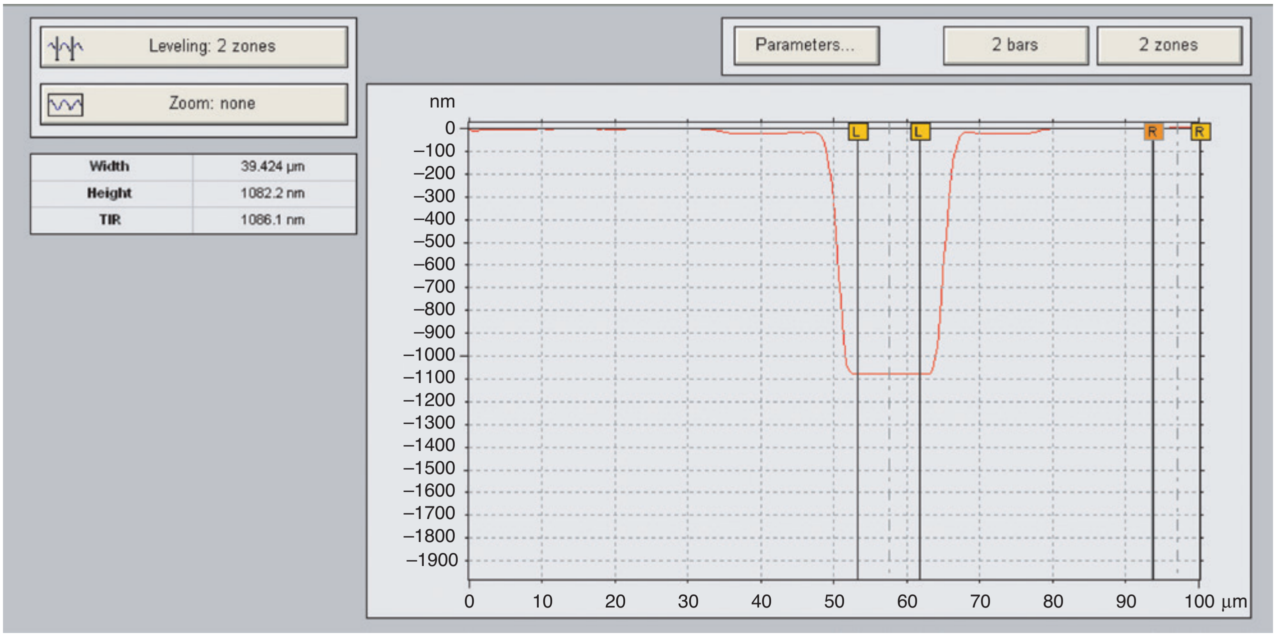

Figure 7: Cross-sectional view of pattern (A).

deepened to approximately 1080 nm. Therefore, the dot pattern on the micro pattern was considered to have been removed by the development. However, when the development process was performed after exposure using the acceleration voltage of 7.5 kV, the dot pattern could be fabricated on the micropattern. Therefore, in subsequent experiments, when a dot pattern was fabricated on a micropattern, development processing was performed separately.

2.3 Fabrication of artificial rose-surface-inspired 3D structure

The EBL design pattern is shown in Figure 8, and Figure 9 presents a schematic illustration of the fabrication method used to obtain the rose petal structure.

On the basis of the results presented in Section 2.1, we selected SML2000 as the resist. Acceleration voltages of 7.5, 10, and 12 kV were used. The EB dose was performed in a region of saturation of the depth characteristic. Rates of 50 µC/cm^2 at 7.5 kV, 100 µC/cm^2 at 10 kV, and 120 µC/cm^2 at 12 kV were used. On the basis of the results presented in Section 2.2, development processing was performed once after micropattern exposure. A dot pattern was exposed to a fabricated micro-pattern area at 20 kV. Then, an EB dose of 180 µC/cm^2 was used. Similarly, the exposed areas were developed using ZED-N50 for 60 s. A superposition method in which the acceleration voltage was changed will be described later. After changing the acceleration voltage, the beam current was measured at the Faraday cup position. After aligning the beam axis of astigmatism, the beam was moved to the reference position by moving the stage. Then, the pattern design diagram made with the BMP file was exposed. These operations were performed each time the acceleration voltage was changed. Because the alignment accuracy of the scanning electron microscope used in this experiment was a maximum of 500 nm, errors occurred in the superposition of the patterns. The exposed areas were developed for 60 s using the ZED-N50.

Next, we obtained a replica pattern using UV-NIL and the fabricated mold. A Cr layer of approximately 30 nm was deposited on the fabricated 3D mold using vacuum evaporation (VPC-260F, Ulvac Kiko, Inc., Japan). The chromium layer was subsequently converted to Cr_2O_3 upon reaction with oxygen upon exposure to air. The presence of the chromium oxide layer improved the effectiveness of the subsequent treatment with a fluorinated silane coupling agent coated on top of the deposited Cr mold. The fabricated mold was coated with a silane coupling agent (Optool DSX; Daikin Industries, Ltd., Japan). A replica pattern of the mold was fabricated using the UV-NIL process. We applied a UV curable resin (PAK-01 CL, Toyo Gosei Co., Ltd., Japan) on a polyester film (Cosmoshine A4300, Toyobo Co., Ltd., Japan). A replica pattern was made using a UV-NIL parallel plate. The NIL pressure was 3.0 MPa, the exposure time was 30 s, and the UV dose was 2.4 J/cm^2. The replica pattern of the mold was also fabricated using silver ink (T10Z-A02 Dowa Electronics Materials Co., Ltd. Japan). Silver ink was placed on the replica and pressed using a roller. Details of the fabrication of the silver duplicated pattern are presented in Figure 10. Silver ink was poured onto the fabricated mold. Then, the poured silver ink was pressed using a roller onto a polyester film at a speed of 1.0 mm/s and a pressure of 1.0 MPa. The film was released, and extra silver ink was removed from the fabricated mold. The mold containing the silver ink was baked at 150°C for 5 min. Next, the silver ink pattern was released from the mold using UV-NIL. UV curable resin (hereafter ETAX, Autex Co., Ltd., Japan) was dropped onto the mold containing silver ink and cured using UV irradiation. Finally, by releasing the mold, we obtained an artificial silver petal pattern on the polyester film.

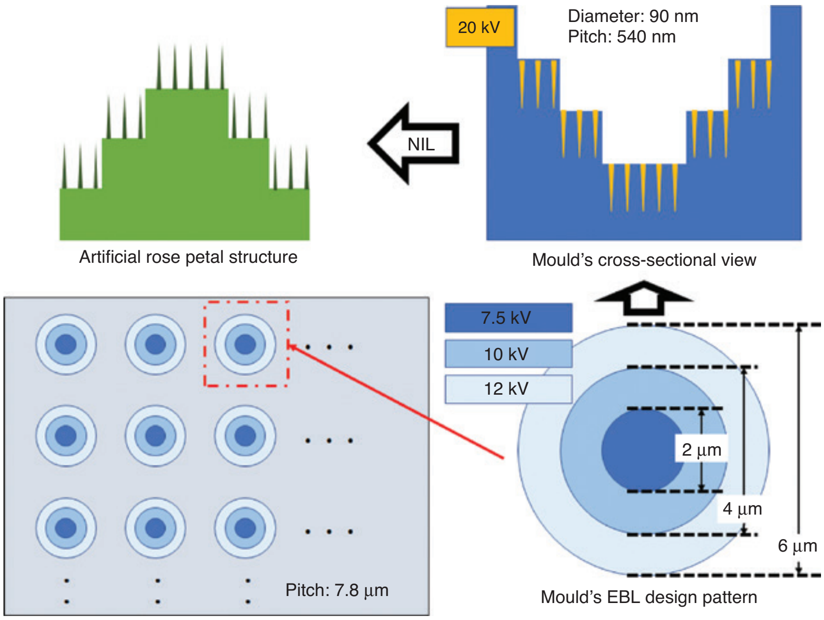

Figure 8: EBL design pattern of mold and target shape.

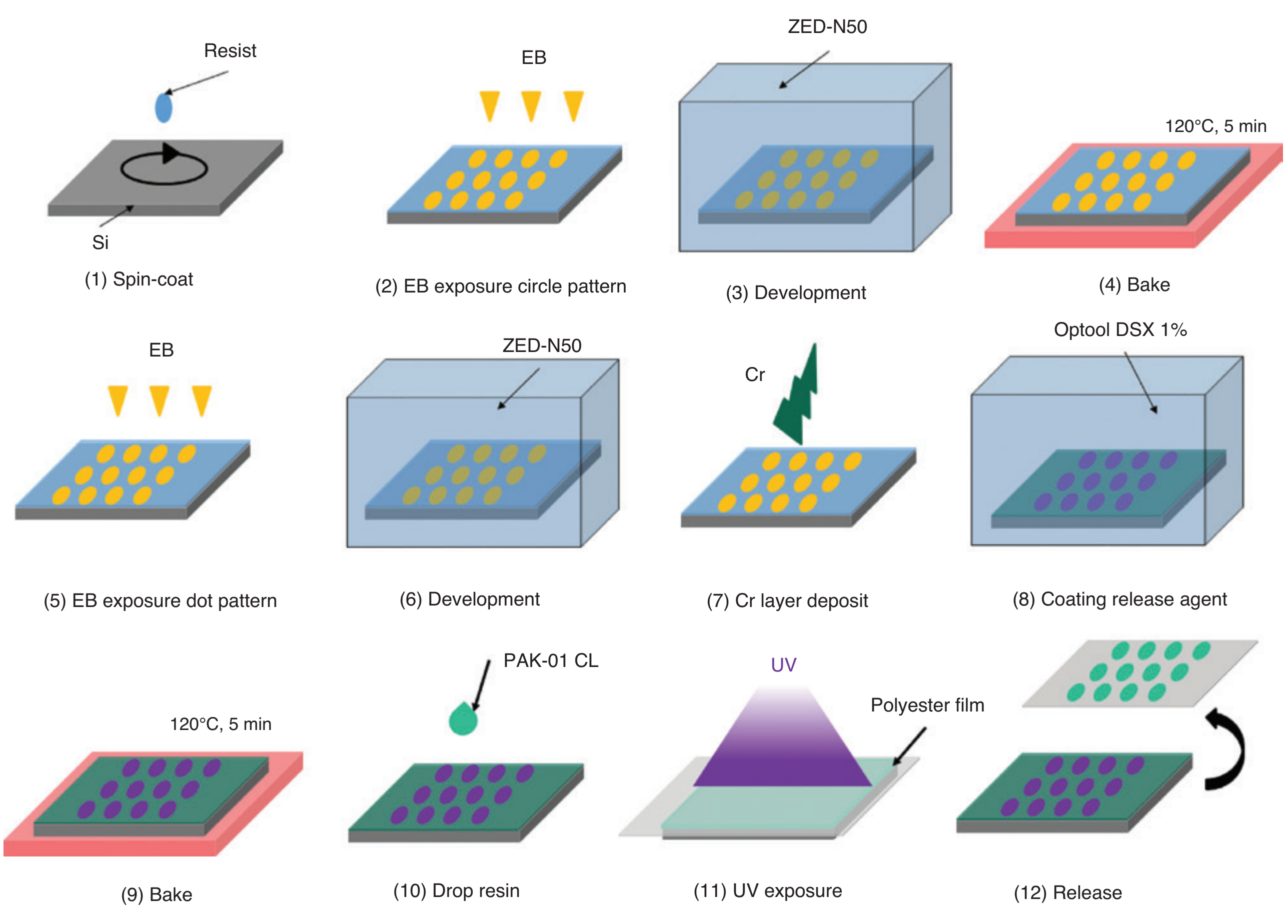

Figure 9: Fabrication method for NIL mold and replica pattern.

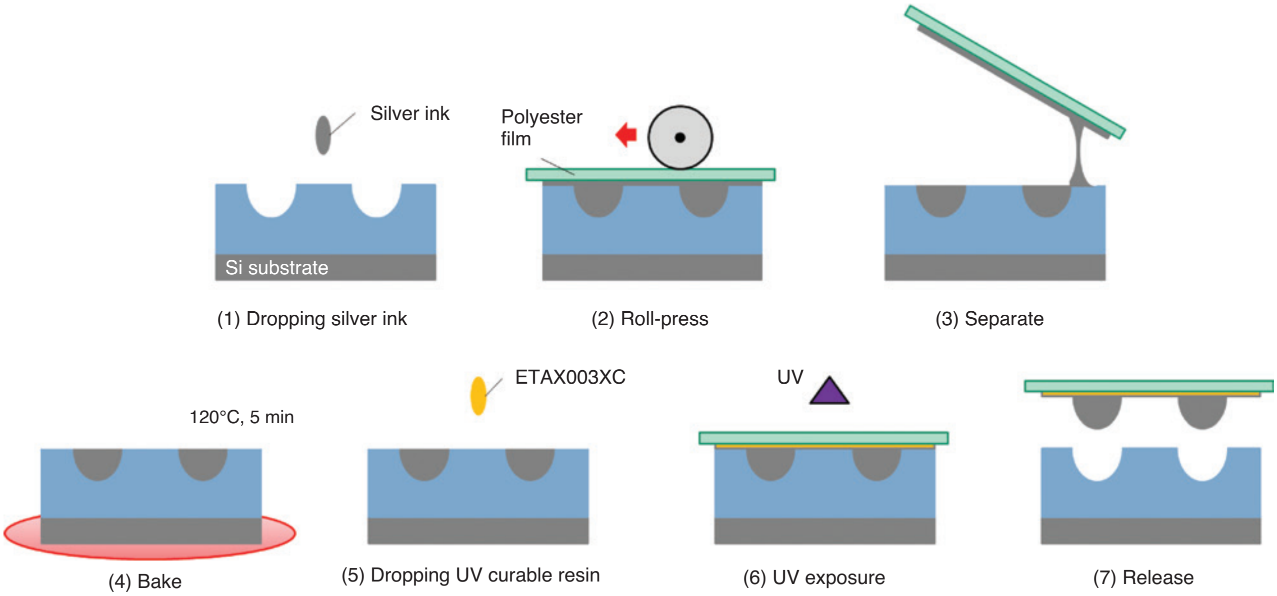

Figure 10: Fabrication of silver duplicated pattern: (1)–(4) filling the mold with silver and (5)–(7) separating silver from the mold.

3 Results and discussion

3.1 Fabrication of artificial rose-surface-inspired 3D structure

A scanning electron microscopy (SEM) image of the fabricated rose petal-inspired NIL mold is presented in Figure 11.

The depths of the pattern were approximately 0.8 µm for the 7.5-kV pattern and 2.0 µm for the 12-kV pattern. According to the characteristic investigation of SML2000, the developing depth at 7.5 kV and 50 µC/cm^2 was 0.8 µm and that at 12 kV and 120 µC/cm^2 was 1.9 µm. These values are almost identical to the measured values. These results indicate that the developing depth could be accurately controlled using the acceleration-voltage modulation method. In addition, according to the measurements, a region with an acceleration voltage of 10 kV did not appear. Thus, the 10-kV pattern between the two accelerations was considered to be affected and gently sloped. The diameter of the micro-circle was approximately 6.9 µm, and the diameter of the nano-dot pattern was approximately 170 nm.

An SEM image of the duplicated pattern is presented in Figure 12.

A nano-dot pattern on a micro-size pattern was obtained using UV-NIL. The height of the 7.5-kV pattern was 0.8 µm and that of the 12-kV pattern was 1.9 µm. Characteristic investigation of SML2000 was 0.8 µm at 7.5-kV pattern and 1.9 µm at 12-kV. Therefore, the measured value is close to the value of the characteristic

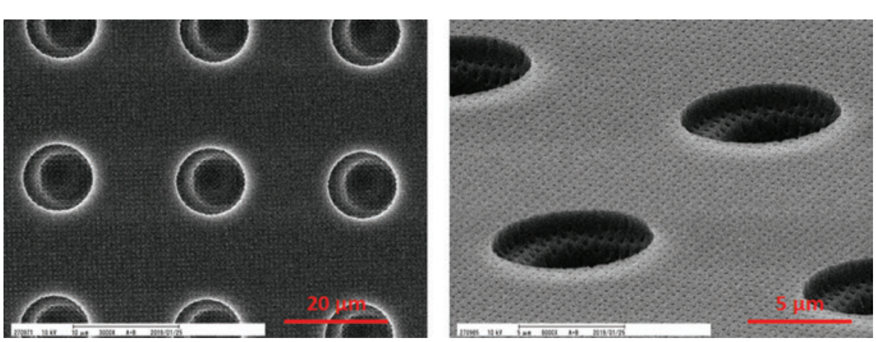

Figure 11: SEM image of resulting fabricated rose petal mold.

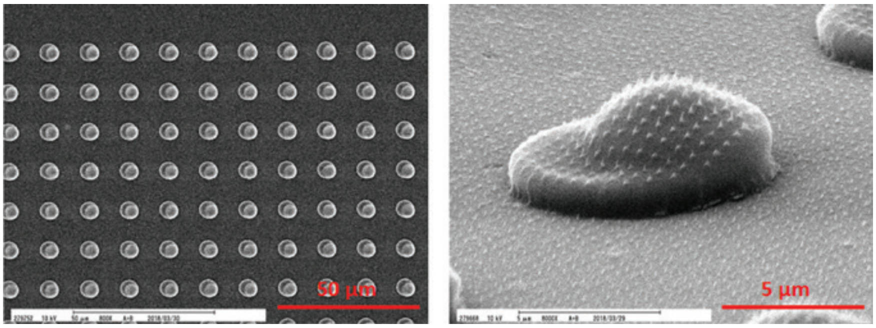

Figure 12: SEM image of the duplicated pattern obtained using UV-NIL.

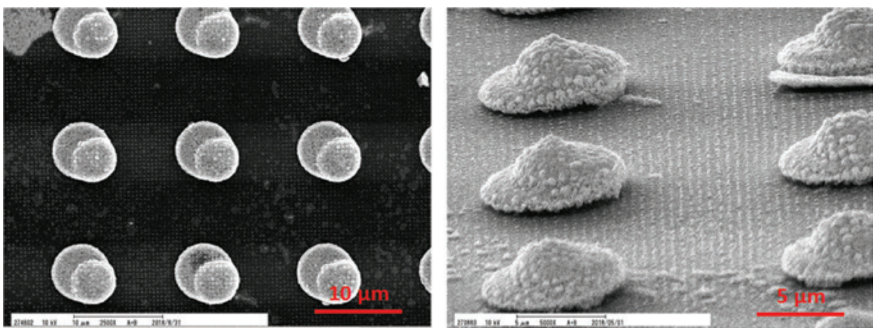

Figure 13: SEM image of resulting duplicated pattern using silver ink.

investigation, and it shows that the developing depth can be controlled by the acceleration-voltage modulation method. The height and diameter of the nano-dot pattern were 110 and 210 nm, respectively. In addition, the diameter of the micro-circle pattern was 7.5 µm. These values are almost equivalent to the shape of the mold. Figure 13 shows the pattern duplicated with silver ink. Thus, we succeeded in fabricating a silver-duplicated pattern using the fabricated 3D mold.

4 Conclusion

First, we examined the characteristic developing depth of CSAR62 and SML2000 as a function of changing acceleration voltage. Because CSAR62 is a thin-film resist, it was difficult to control the depth using the dose-modulation method because the developing depth changed greatly with a low dose amount. However, if the developing depth at low acceleration voltage was saturated, control of the developing depth became easy using acceleration-voltage modulation. The thickness of the SML 2000 film was 3000 nm, and relatively thick samples could be prepared using EB. Therefore, this resist was considered suitable for 3D structure fabrication.

We then fabricated 3D micro-nano hybrid structures using acceleration-voltage modulation. When simultaneously exposing acceleration voltages of 7.5 and 20 kV, it was impossible to fabricate a dot pattern on the micro pattern. However, when the development process was performed after exposure using an acceleration voltage of 10 kV, the dot pattern could be fabricated on the micropattern.

Finally, we fabricated a rose petal-inspired 3D mold using the characteristic of developing depth of SML2000. An artificial rose petal mold was fabricated using four acceleration voltages. We successfully fabricated nano dot patterns on micro hole patterns. The depths of the mold were similar to the characteristics of the electron penetration depths. These results indicate that it is possible to fabricate a more precisely controlled 3D structure using the acceleration-voltage-modulation method. In this study, the fabricated mold had some steps. However, we believe that it is possible to make a smooth shape using various acceleration voltages. In addition, the duplicated pattern was obtained using UV-NIL and the fabricated 3D mold. The obtained duplicated patterns had 3D structures similar to the shape of the fabricated mold. We also succeeded in fabricating a silver duplicated pattern using the fabricated 3D mold. Our findings demonstrate that various complex 3D structures using various materials can be fabricated using the acceleration-voltage-modulation method and NIL.

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