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Preparation of Diamond Mold Using Electron Beam Lithography for Application to Nanoimprint Lithography

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Diamond molds were fabricated by two types of fabrication processes, both of which use a conductive intermediate layer between the diamond surface and polymethylmethacrylate (PMMA) resist to prevent surface charge-up. Using a PtPd intermediate layer, electron beam lithography and ion beam etching, a denting line pattern of 600 nm width and 70 nm depth was fabricated. Using a carbon intermediate layer, electron beam lithography, PtPd lift-off and oxygen ion beam etching, a convex line pattern of 600 nm width and 110 nm height was fabricated. These diamond molds were pressed into PMMA on a silicon substrate that was heated to a temperature of 150°C and kept at a pressure of 23.5 MPa until the temperature dropped below 90°C, and then the diamond mold was released from the PMMA. The convex line pattern of 600 nm width and 150 nm height was imprinted using a denting diamond mold. The denting pattern of 1100 nm width and 180 nm height was imprinted using a convex diamond mold. PMMA patterns were transferred well over the imprinted area by the diamond molds.

KEYWORDS: nanoimprint lithography, diamond mold, polymethylmethacrylate, lift-off, atomic force microscope

1. Introduction

As silicon LSI devices continue to be scaled down in size, the patterning process of resists on Si wafers is becoming more critical. For Si LSI, a reliable lithographic technology is needed to define features with dimensions below 0.1 μm. Recently, numerous promising lithographic technologies which can delineate feature dimension size in the sub-μm region have been proposed. However, next-generation lithographic technology requires not only high resolution but also high throughput, large process latitude and low cost. Optical lithography becomes more difficult when the feature size goes below 0.2 μm.[1] For direct electron beam lithography, the throughput and process latitude have to be increased to realize practical mass production.[2,3] Both X-ray and ion beam lithography still require further development in the areas of the exposure system and mask technology.[4,5] Nanoimprint lithography (NIL) is a major breakthrough in nano-patterning because it can produce sub-μm feature size over a large area with a high throughput and low cost.[6] NIL yields a resist pattern by deforming the resist shape on the substrate by the compression of the nanoscale pattern delineated mold. Chou *et al.* reported the performance of NIL using SiO_2 molds and polymethylmethacrylate (PMMA) at high temperatures for microelectronics[6,7] and magnetic disks.[8] This lithography technique uses the physical contact of a mold with a substrate surface, thus, breakage and distortion of mold patterns at the time of contact or during repeated runs of the NIL process are serious problems for repeatability and productivity. In order to realize high productivity, the necessary condition for mass production, the mold is required to be durable for repeated runs of the NIL process and strong at the time of contact with the substrate. Diamond is a candidate material for realizing high productivity, as it has numerous superior properties such as large Knoop hardness, large compressive strength, large tensile strength, high thermal conductivity and low thermal expansion coefficient. These properties are ideal for thermal cycle nanoimprint lithography. Therefore, we fabricated a diamond mold using the electron beam lithography technique. Furthermore, using a diamond mold instead of the diamond indenter of a conventional hardness tester, direct nanoimprinting becomes possible. In this case, nanoimprinting experiments were easily carried out. Diamond is an electrical insulator, so resist patterns on diamond are distorted by electron beam exposure because of charge-up of the diamond surface. In order to prevent charge-up and delineate fine line-and-space patterns, we carried out two types of diamond mold fabrication processes, both of which use a conductive layer on the diamond surface. Using a diamond mold, successful pattern transfer to PMMA on Si substrates was realized.

2. Experimental Apparatus and Procedure

Synthetic single-crystal diamonds with (100) oriented face were used as the mold. A Kaufman-type ion source was used for etching of the diamond because this equipment can perform anisotropic etching and generate an argon ion beam and an oxygen ion beam with a large area of uniform ion beam density. The positive type PMMA resist was used as an electron beam (EB) resist. Using this resist, only a positive tone diamond mold was obtained. However, to compare the mold shapes and pattern transfers, a negative tone diamond mold is also required. In order to obtain a two-type tone diamond mold and to prevent diamond surface charge-up, the following two fabrication processes, both of which use a conductive intermediate layer between the diamond surface and resist, were performed. One process involved utilizing a PtPd intermediate layer and the other process utilized a carbon layer. The reason why we selected these two materials is that the conventional surface coater, used for the preparation of high-resistivity specimens for scanning electron microscope (SEM), utilizes PtPd and carbon. Oxygen ion beam etching was carried out for etching of diamond, because the etching rate of the oxygen ion beam was five times faster than that of an argon ion beam under the same etching conditions. The etching rate ratio of oxygen ion beam etching under the same etching conditions was PMMA:C:PtPd:diamond=10:10:1:1.

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Thus, the PtPd layer was used as the etching mask from oxygen ion beam irradiation. The diamond mold fabrication process using a PtPd intermediate layer is shown in Fig. 1 (PMMA/PtPd/diamond process). In order to prevent diamond surface charge-up, PtPd was deposited on the diamond surface by a conventional sputter coater, then PMMA resist was spin coated (Fig. 1(1)). PMMA is present on the top layer of this sample, thus, fine patterning of this layer was performed by EB lithography, after PMMA was prebaked at 170°C for 30 min. (Fig. 1(2)). PMMA was developed in a mixture of MIBK:IPA=1:3 (Fig. 1(3)). We selected argon ion beam etching for etching of the PtPd layer and PMMA, because the selectivity (PtPd etching rate/ PMMA etching rate) was higher than that of oxygen ion beam etching. The selectivity values of argon ion etching and oxygen ion etching were 0.29 and 0.10, respectively. The argon ion beam was bombarded on the sample; subsequently, both the PMMA layer and bare PtPd layer after removal of the PMMA layer were etched by physical sputtering. By this process, PMMA patterns were transferred into the PtPd layer and the PMMA layer was etched away (Fig. 1(4)). Diamond was etched by oxygen ion beam bombardment, and then the PtPd layer acted as a mask (Fig. 1(5)). When the PtPd layer was etched away, the diamond mold was fabricated (Fig. 1(6)). The carbon intermediate layer process is shown in Fig. 2 (PMMA/C/diamond, PtPd lift-off process). In order to prevent diamond surface charge-up, carbon was deposited on the diamond surface by a carbon evaporator, then the PMMA resist was spin coated (Fig. 2(1)). After PMMA was prebaked, the sample was exposed by EB (Fig. 2(2)) and PMMA was developed (Fig. 2(3)) in the same way as in the PMMA/PtPd/diamond process. Next, PtPd was deposited on this sample (Fig. 2(4)) and PMMA was lifted off by acetone (Fig. 2(5)), and PtPd patterns remained. Finally, an oxygen ion beam was irradiated to etch the diamond using the PtPd mask (Fig. 2(6)). As shown in the NIL process in Fig. 3, the diamond mold was pressed into PMMA on a silicon substrate that was heated above its glass transition temperature (105°C). Above this temperature, PMMA behaves as a viscous liquid and can flow under pressure, thereby conforming to the diamond mold. The diamond mold was pressed against PMMA and the pressure was maintained until the temperature dropped below the PMMA transition temperature. After that, the diamond mold was released from PMMA. The etched depths in the diamond molds and the

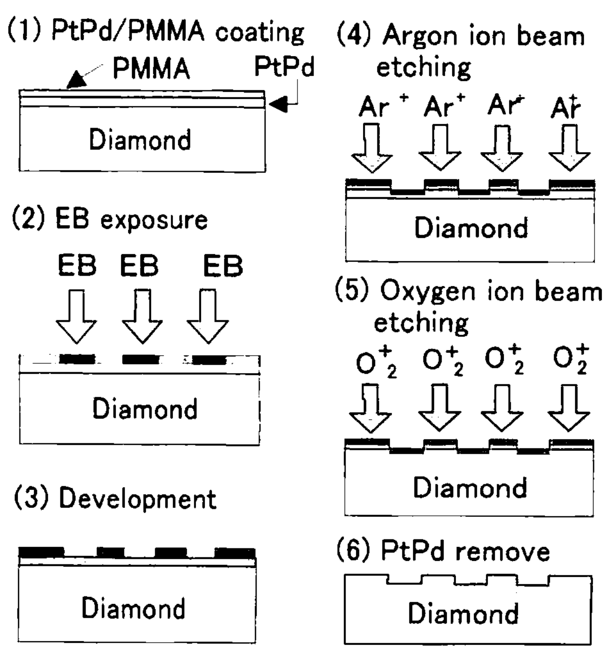

Fig. 1. Fabrication process of diamond mold using a PtPd intermediate layer (PMMA/PtPd/diamond process).

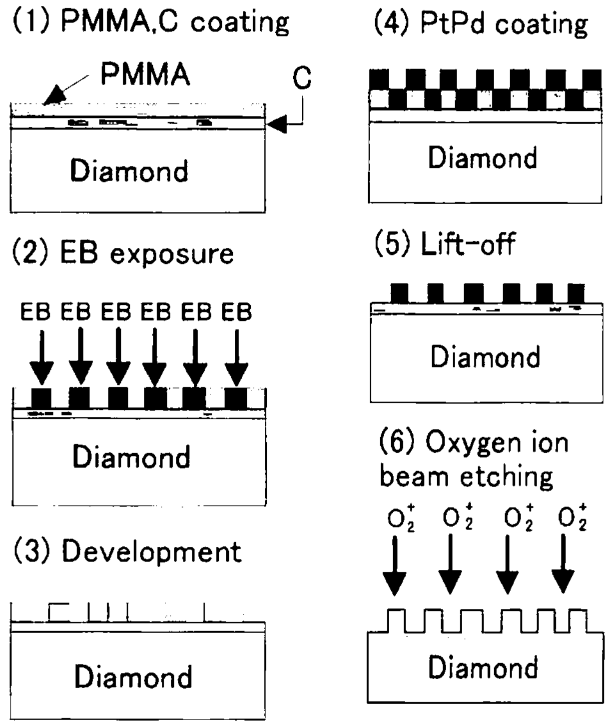

Fig. 2. Fabrication process of diamond mold using a carbon intermediate layer (PMMA/C/diamond process).

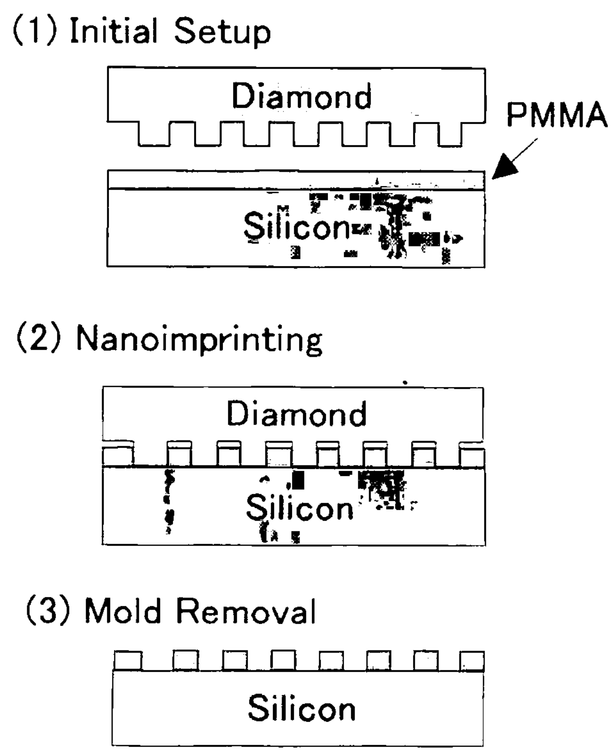

Fig. 3. Schematic of nanoimprint lithography process.

imprinted depths in PMMA patterns were evaluated using an atomic force microscope (AFM).

3. Experimental Results and Discussion

3.1 Fabrication of diamond mold

First, we tried EB lithography using only a PMMA resist without any intermediate layer. However, distorted PMMA line patterns were obtained on diamond (Fig. 4). The reason for this is considered to be as follows. When the primary electron impinges on PMMA, secondary electrons are generated and spread into PMMA. Diamond resistivity is very high (over 10 GΩ cm), thus these secondary electrons remain on the diamond surface, and the charge-up phenomenon occurs at the PMMA resist surface. Therefore, we used an intermediate layer between PMMA and the diamond surface to prevent charge-up and to fabricate straight patterns. Fabrication of the diamond mold using the PMMA/PtPd/diamond process (see Fig. 1) was carried out under the following conditions. Thicknesses of PtPd and PMMA layers were 100 nm and 300 nm, respectively. The EB lithography conditions were a 20 kV accelerating voltage, 3 nA beam current and 0.3 μm beam diameter. The argon ion beam bombardment conditions were a 1 kV accelerating voltage, 0.13 mA/cm^2 ion beam density and 40 min etching time. The oxygen ion beam bombardment conditions were a 1 kV accelerating voltage, 0.13 mA/cm^2 ion beam density and 90 min etching time. The AFM image of this diamond mold and cross-sectional profile of the etched line are shown in Figs. 5(a) and 5(b), respectively. As shown in Fig. 5, a dented line pattern of 600 nm width and 70 nm depth was fabricated. Fabrication of the diamond mold using the PMMA/C/diamond process (see Fig. 2) was carried out under the following conditions. Thicknesses of car-

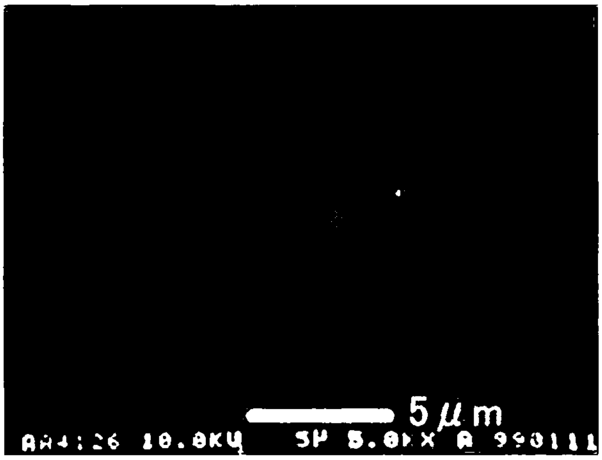

Fig. 4. SEM micrograph of the distorted PMMA line patterns on diamond.

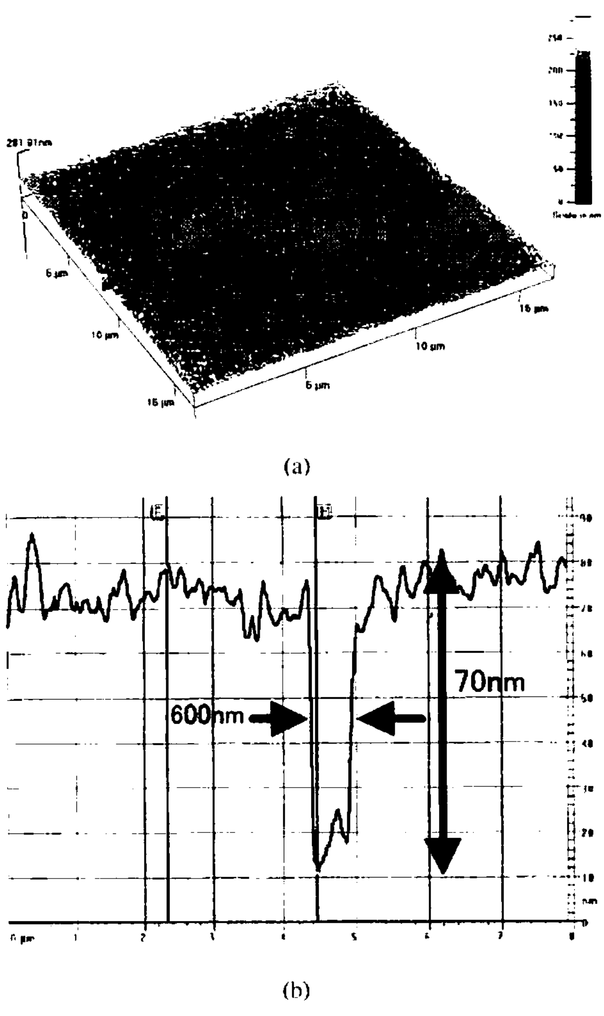

Fig. 5. AFM image of diamond mold fabricated using the PMMA/PtPd/ diamond process (a) and cross-sectional profile of etched line (b).

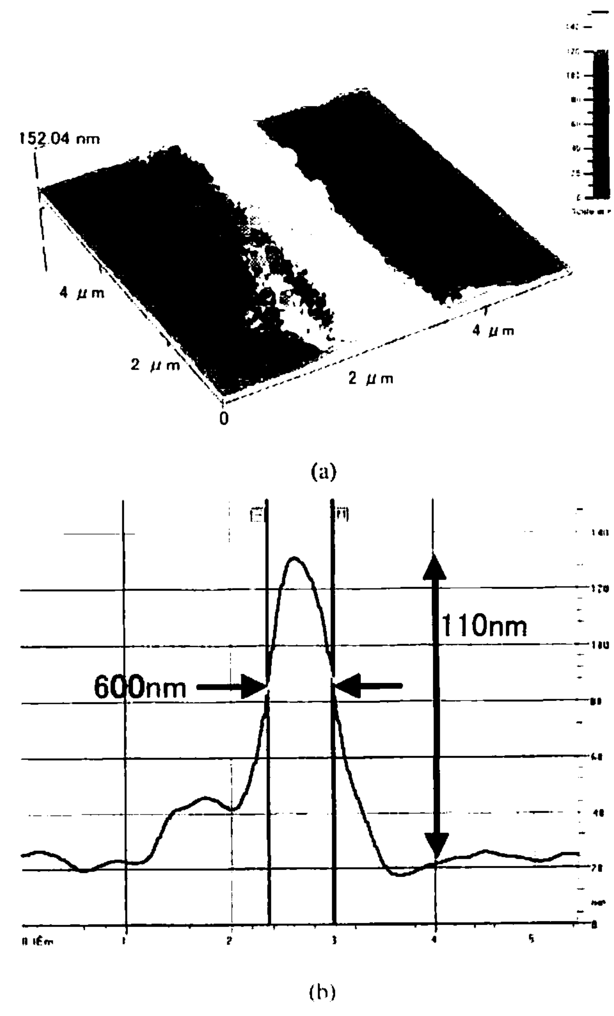

Fig. 6. AFM image of diamond mold fabricated using the PMMA/C/ diamond process (a) and cross-sectional profile of etched line (b).

bon and PMMA were 170 nm and 300 nm, respectively. The EB lithography conditions were a 20 kV accelerating voltage, 3 nA beam current and 0.3 μm beam diameter. The thickness of PtPd was 100 nm. The oxygen ion beam bombardment conditions were a 1 kV accelerating voltage, 0.13 mA/cm^2 ion beam density and 60 min etching time. The AFM image of this diamond mold and cross-sectional profile of the etched line are shown in Figs. 6(a) and 6(b), respectively. As shown in Fig. 6, a convex line pattern of 600 nm width and 110 nm height was fabricated. Both processes can delineate straight patterns, which suggests both processes are effective in preventing diamond surface charge-up and in the fabrication of diamond molds.

3.2 *Imprinted PMMA patterns by diamond molds*

A diamond mold was pressed into PMMA on a silicon substrate that was heated to a temperature of 150°C and kept at a pressure of 23.5 MPa for 40 min until the temperature dropped below 90°C. The diamond mold was then released from PMMA. The AFM image of the PMMA pattern imprinted on the Si substrate by the denting line pattern mold and its cross-sectional profile are shown in Figs. 7(a) and 7(b), respectively. As shown in Fig. 7, a convex line pattern of 600 nm width and 150 nm height was fabricated. However, for the part of the line in Fig. 7 which corresponds to that in Fig. 5, the height is larger than the mold depth. The reason for this is considered to be as follows. When the mold was released from PMMA at the temperature of 90°C, PMMA was still a high-viscosity liquid. Thus, the capillary phenomenon occurred between the dented parts of the mold surface and the PMMA liquid and PMMA travelled up along the sidewalls of the dented parts. Therefore, the height of the transferred PMMA pattern which should correspond to the dented part of the mold is larger than the depth of the diamond mold. The AFM image of PMMA pattern imprinted on the Si substrate by the convex line pattern mold and its cross-sectional profile are shown in Figs. 8(a) and 8(b), respectively. As shown in Fig. 8, the dented pattern of 1100 nm width and 180 nm depth was fabricated. This time, the depth and width are larger than the mold height and width. The reason why the transferred PMMA depth is larger than the mold height is the same as that given above. The reason why the transferred PMMA width is larger than the mold width is considered to be that when the mold was released from the PMMA, the convex parts of the mold moved slightly toward the side. In this case, the convex area of the mold was small, and thus it might tend to shift with the movement at the time of release. Although there was a little distortion of the imprinted patterns, generally, the imprinted PMMA patterns were transferred well over the im-

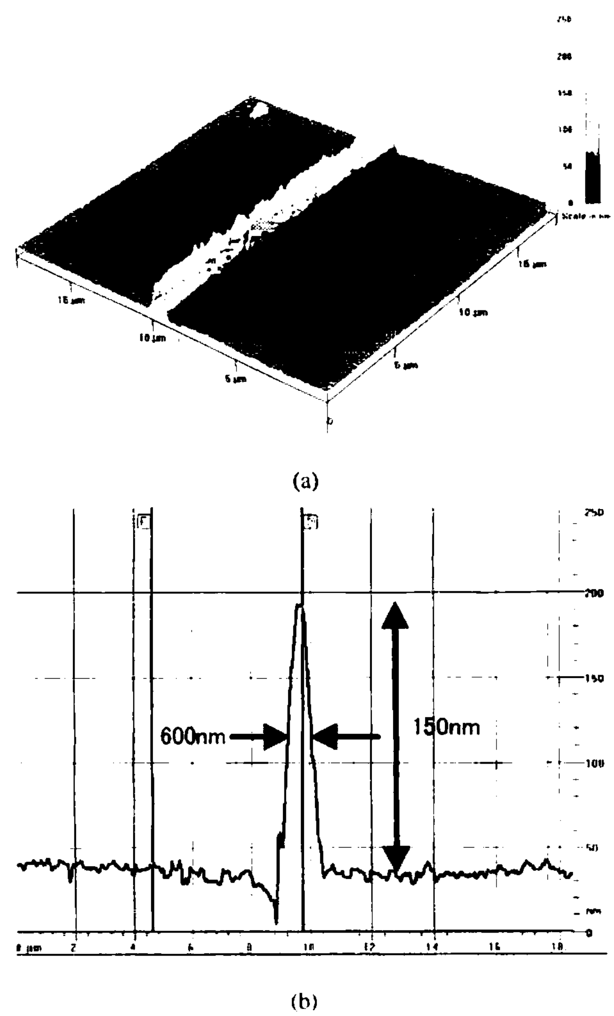

Fig. 7. AFM image of imprinted PMMA pattern on Si substrate by denting line pattern mold (a) and cross-sectional profile of imprinted PMMA pattern (b).

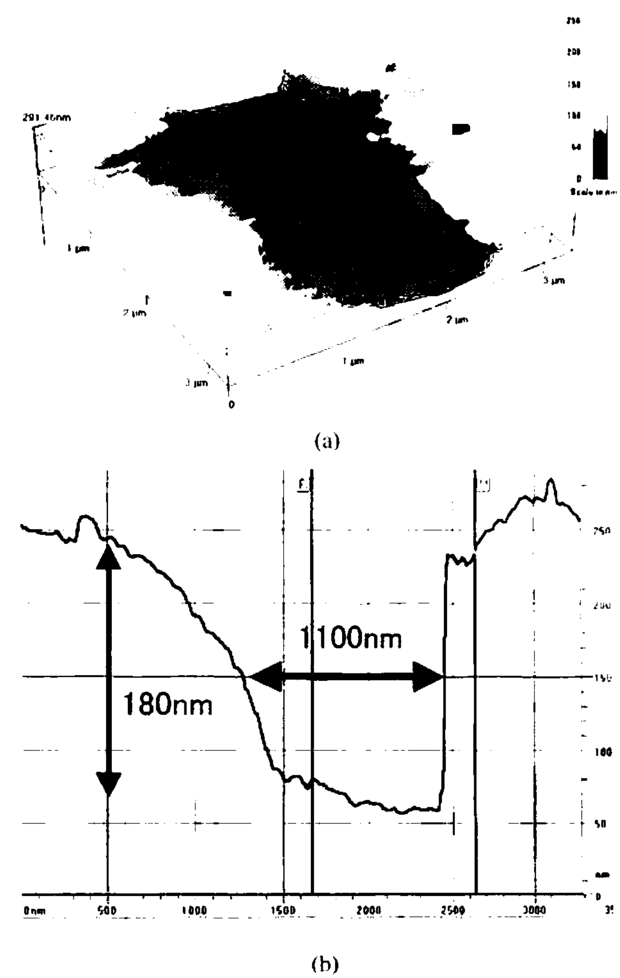

Fig. 8. AFM image of imprinted PMMA pattern on Si substrate by convex line pattern mold (a) and cross-sectional profile of imprinted PMMA pattern (b).

printed area. Therefore, diamond molds were suitable for NIL using a PMMA resist. In order to obtain imprinted patterns without distortion, further investigation of imprint conditions and fabrication of smaller-pattern diamond molds with a high aspect ratio are necessary. Moreover, the endurance testing of the diamond mold is necessary to ensure the realization of high productivity when using NIL.

4. Conclusion

In order to obtain fine patterns and an anisotropic-shape diamond mold, we selected EB lithography and ion beam etching, respectively. Distorted patterns were obtained when the PMMA/diamond was exposed by EB because of the occurrence of surface charge-up. In order to prevent the surface charge-up and to fabricate a two-type tone diamond mold using PMMA EB resist, the following two fabrication processes, both of which use a conductive intermediate layer between the diamond surface and resist, were established. One process utilized a PtPd intermediate layer and the other process utilized a carbon layer. Using the PtPd intermediate layer, a dented line pattern of 600 nm width and 70 nm depth was obtained. Using the carbon intermediate layer, a convex line pattern of 600 nm width and 110 nm height was fabricated. The desired patterns were transferred to PMMA on the Si substrate, when diamond molds were pressed into PMMA that was heated to the temperature of 150°C and maintained at a pressure of 23.5 MPa. Using the denting diamond mold, a convex pattern of 600 nm width and 150 nm height was fabricated. Using the convex diamond mold, a dented pattern of 1100 nm width and 180 nm depth was fabricated. Diamond molds were suitable for NIL using a PMMA resist.

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