PENETRATION OF RESIDUAL LAYER IN NANOIMPRESS LITHOGRAPHY BY DIRECT OXIDATION OF PHOTOCATALYTIC FILM

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INTRODUCTION
The demand for the practical use of the nanoimprint lithography (NIL) has risen for the miniaturization in two-dimensional micro/nano fabrication technology. Photolithography is now used widely, however, has a few of difficulties such as the high equipment cost and the diffraction limit. NIL, in which a resist on a substrate is patterned by mechanical pressing a nanostructured mold, is expected to be a post-technology of photolithography [1]. However, in order to use NIL practically, there is a problem of residual layer. Residual layer is the part of resist which is remained in the convex part of mold by the viscosity in arranging resist by the nanoimprint. Then the process of O₂-plasma etching is needed to remove residual layer in processing the substrate and this process causes a side etching.

FIGURE 1. Schematic of the side etching.

MECHANISM OF OXIDATION OF PHOTOCATYALYST
Figure 2 shows the remote oxidation mechanism of photocatalyst [2]; Free electrons and holes are generated by TiO₂ under UV irradiation (FIG 2b). A H₂O₂ travels to the substrate by diffusion (FIG 2e). A hydroxyl radical is produced from a H₂O₂ under UV irradiation (FIG 2f, 2g). Resist is oxidized and decomposed by oxidation of Hydroxyl radicals (FIG 2h) [3]. Photocatalytic lithography in 100 μm order has been demonstrated using remote oxidation [4][5].

FIGURE 2. Remote oxidation mechanism of photocatalyst.

PROPOSAL OF METHOD OF PENETRATION OF PHOTOCATYALYST
In this paper we propose a method to penetrate the residual layer by direct oxidation of photocatalytic film. The remote oxidation is an isotropic etching and the diffusion of H₂O₂ reaches about 100 μm. Because of the isotropy, the groove broadens as wide as the resist thickness. On the other hand, the direct oxidation of residual layer after nanoimprint minimized the broadening of groove width (FIG 3). Pattern will be destructed around TiO₂ film as maximum residual layer thickness. So, TiO₂ should be arranged only in the convex parts of mold to make TiO₂ film thickness thin.
FIGURE 3. Conceptual diagram of Pattern destruction;
(a) photocatalytic lithography, (b) NIL with the penetration of residual layer.

Figure 4 shows the conceptual diagram of penetration of residual layer. Nanoimprint is done using the quartz mold with micro/nano patterns of which TiO$_2$ is arranged in the convex parts (FIG 4b). The resist nearly TiO$_2$ film is decomposed under UV irradiation from the mold (FIG 4c, 4d). Mold is released (FIG 4e).

FIGURE 4. Conceptual diagram of the method to penetrate the residual layer.

FABRICATION OF MOLD
The molds were fabricated as follows (FIG 5);
Quartz plates were cleaned by ultrasonic bath with acetone, with ethanol and then with deionized water for 5 min. respectively.

FIGURE 5. Process of fabrication of mold.

Ti was sputtered 100nm by magnetron sputtering (FIG 5b). The sputtering condition was decided according to other reports [6][7][8]. Resist was arranged in 1- and 2-μm-pitch line-and-space patterns by electron beam(EB) lithography (FIG 5c, 5d). Cr was sputtered 800nm and Cr on the resist was removed by lift-off (FIG 5e, 5f). The quartz plates and TiO$_2$ film were etched using arranged Cr as mask by Inductive-coupled-plasma reactive ion etching (ICP-RIE) (FIG 5g, 5h). The etching conditions are listed in Table 2. Cr was removed using etchants (FIG 5i). Figure 6 shows the schematic of the mold and figures 7(a1-b2) show the scanning electron microscopy (SEM, Hitachi S-4000) images.

TABLE 1. Etching conditions.

<table>
<thead>
<tr>
<th>Etching gas</th>
<th>CHF$_3$</th>
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<tbody>
<tr>
<td>Antenna power (W)</td>
<td>400</td>
</tr>
<tr>
<td>Bias power (W)</td>
<td>150</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>1</td>
</tr>
<tr>
<td>Etching rate of Ti (nm/min)</td>
<td>60</td>
</tr>
<tr>
<td>Etching rate of SiO$_2$ (nm/min)</td>
<td>240</td>
</tr>
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FIGURE 6. Schematic of the mold.
FIGURE 7. SEM image of the mold with 1-μm-depth and 1- and 2-μm-pitch line-and-space patterns which 200-nm-thick TiO$_2$ is arranged in the convex parts of. tilt: 30 degree. (a1) (a2) 2-μm-pitch, (b1) (b2) 1-μm-pitch.

The result of X-ray diffraction (XRD) analysis of TiO$_2$ film is shown in Figure 8. The sputtering conditions are listed in Table 2. In the XRD pattern, the diffraction peak of anatase was observed; anatase is one of the several crystal structures of TiO$_2$ and known as photocatalyst.

FIGURE 8. XRD pattern of TiO$_2$; (a) Obtained spectrum, (b) Reference spectrum.

<table>
<thead>
<tr>
<th>TABLE 2. Sputtering conditions of TiO$_2$</th>
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<tbody>
<tr>
<td>Target</td>
</tr>
<tr>
<td>O$_2$ (sccm)</td>
</tr>
<tr>
<td>Ar (sccm)</td>
</tr>
<tr>
<td>Sputtering power (W)</td>
</tr>
<tr>
<td>Substrate temperature (degree)</td>
</tr>
<tr>
<td>Deposition rate (nm/min)</td>
</tr>
<tr>
<td>Sputtering pressure (Pa)</td>
</tr>
</tbody>
</table>

EXPERIMENTAL METHODS
Substrates were fabricated as follows: 1) Si substrates cleaned by ultrasonic bath with acetone, with ethanol and then with deionized water for 5 min. respectively. 2) Polymethylmethacrylate (PMMA) was dissolved in toluene, which concentration is 5mg/l, and spin coated at 2000rpm for 35 sec on the Si plates. The thickness of the PMMA film was 5 nm.

The substrates with TiO$_2$ were exposed to UV ramp for 1-3 hours (FIG 9). The spectrum pattern of the UV ramp is shown in figure 10.

FIGURE 9. Schematic of the exposure experiment.

FIGURE 10. Spectrum pattern of the UV light.

EXPERIMENTAL RESULTS AND DISCUSSIONS
PMMA on Si substrate was resolved using oxidation of TiO$_2$. Figure 11 shows the SEM images of the surface of PMMA film and the
The change of surface structure was observed in the area with TiO₂.

Figure 12 shows the energy dispersive X-ray spectrometry (EDX) results of C/Si atomic ratio as a function of UV exposure time. The decrease of C/Si atomic ratio is observed with longer exposure time at only the area with TiO₂. This means that the change of surface structure was caused by the decomposition of PMMA.

CONCLUSIONS
In this paper we have proposed “the penetration of the residual layer” method for nanoimprint lithography. We successfully fabricated the mold with 1-μm-depth and 1- and 2-μm-pitch line-and-space patterns of which 100-nm-thick TiO₂ is arranged in the convex parts. We confirmed the oxidation of PMMA resist by TiO₂ film.

ACKNOWLEDGEMENT
The mold were made using EB writer (F5112+VD01) donated by ADVANTECH Corporation and ICP-RIE (ULVAC CE300I) in the University of Tokyo VLSI Design and Education Center (VDEC).

REFERENCES