Organic-Inorganic Hybrid Type Electron Beam Resist

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1. Introduction
Analogue resists, defined as resists with given film thickness proportional to exposure dose, are desirable to fabricate optical elements by direct-writing electron beam (EB) lithography.[1,2] The pattern formed by the EB lithography may be transferred to the underlying quartz glass plate by reactive ion etching (RIE), and metal thin film may be deposited on the surface of the pattern.[2] The patterning of quartz glass and metal could potentially be applied to fabrication of diffractive optical elements such as blazed grating. PMMA (OEOR) and P(methyl α-chloroacrylate-co-α-methylstyrene) (ZEP) are commercially available positive type EB resists.[3] The direct EB lithography on PMMA gives diffractive optical elements.[2] However, PMMA does not have sufficient compatibility with quartz and resistance for RIE and heating, which are desirable for fabricating quartz- or metal optical elements via the RIE or metal vacuum-deposition. ZEP has higher EB sensitivity and RIE resistance than OEOR, however, its high γ-value is not suitable for an analogue resist.[4]

Organic-inorganic hybrid materials with molecularly dispersed domains in organic polymer or inorganic matrix have been of interest as a group of new functional materials. We have already reported that sol-gel process of organic polymers and tetraethoxysilane (TEOS) as a precursor of silica matrix affords the hybrids such as polysilane-silica hybrid and acrylic-silica hybrid.[5]

We now report the EB resist of organic-inorganic hybrid thin film for fabrication of optical elements. It is expected that the organic polymer component is EB sensitive and resists RIE, and silica matrix plays the role of heat resistance and compatibility with the underlying quartz. In this study, acrylic polymer (1, Scheme 1) and polysilane-acryl block copolymer (2) were selected as the organic polymers for the precursor of the organic-inorganic hybrid. These acrylic polymers were modified by silica matrix and polysilane segment (silicon modified acrylic polymer; SIMAC) to afford the hybrid thin films.

2. Method
Organic polymers (1a-e, Scheme 1) having trimethoxysilyl group for the precursor of the organic-inorganic hybrid were synthesized by radical polymerization using azo-compounds as the initiators: 1a, Mn = 3.0 x 10^3, M_w/M_n = 1.43; 1b, Mn = 2.21 x 10^3, M_w/M_n = 1.44; 1c, Mn = 3.2 x 10^3, M_w/M_n = 1.87; 1d, Mn = 5.82 x 10^3, M_w/M_n = 2.24; 1e, Mn = 2.42 x 10^3, M_w/M_n = 2.31. Also the photopolymerization was carried out using the polymethylphenylsilane (PMPS, Mn = 1.32 x 10^4, M_w/M_n = 1.94) as a macromolecular photo-radical initiator to afford block copolymer 2 (Mn = 1.02 x 10^4, M_w/M_n = 1.78).[5]
Propylene glycol 1-monomethyl ether 2-acetate (PEGMA) solution of the polymers, TEOS and a catalytic amount of HCl was spin-coated on a quartz glass plate, followed by heating at 120°C for 2h under air atmosphere, giving the hybrid thin film (thickness 0.05 - 0.2 µm). The thin film was not soluble in PEGMA and was transparent and crack-free. Similar spin-coating from the polymer solution of 1 or 2 without TEOS also gave the thin films consisted of the cross-linked organic polymers.

The EB lithography was carried out using a JEOL JBX-5000SIL. Then the thin films were irradiated with EB of which acceleration voltage was 50 kV. The test pattern was written on the thin film. Then the film was developed by 2-propanol / 2-butanone (1:1) for 60 sec and was observed by a laser interference microscope ZYGO. Spin-coating films of PMMA (OEBR-1000, Tokyo Ohka Co.), ZEP (ZEP-520-22, Nippon Zeon Co.) and PMPS were also evaluated as references.

The fluorocarbon/O2 reactive ion etching (RIE) was carried out using a ULVAC NLD-800. The etching conditions were as follows: antenna power of 1500 W, bias power of 400 W, pressure of 0.6 Pa, etching time of 1 min, C4F8 flow of 16 sccm, CH2F2 flow of 14 sccm, and O2 flow of 3 sccm. The etching rate of quartz was 0.68 µm min⁻¹. Relative etching resistance of the resists against quartz as a reference substrate was defined as RIE selectivity (Table 1).

3. Result and Discussion
The EB lithography of 1/TEOS or 2/TEOS hybrid films afforded positive pattern whose depth, i.e., resist film thickness, corresponded to EB exposure dose, indicating that those hybrids were classified as analogue resists. The 1.0 µm L/S was observed by ZYGO. Sensitivity and υ-value were obtained from the plot of dose and positive pattern depth (Table 1, Figure 1). The positive pattern was transferred to the underlying quartz glass plate by RIE. The RIE selectivity (relative etching resistance of the hybrids against quartz as a reference) is shown in Table 1. The EB lithography results of spin-coating films of cross-linked 1a-e, PMMA, ZEP and PMPS are also shown there.
ZEP as a reference EB resist is a copolymer of methyl α-chloroacrylate and α-methylstyrene. It is expected that the α-chloro group and the phenyl group contribute toward increasing the EB sensitivity and RIE resistance, respectively.[4]

Both functional groups also seem to play important roles to improve the EB sensitivity and RIE resistance of the hybrids. The hybrids from 1/TEOS and 2/TEOS had higher etching resistance than PMMA. The 1a/TEOS hybrid had higher RIE resistance than 1a, although silica matrix was expected to exhibit similar etching resistance to that of quartz. It should be emphasized that the phenyl group in the hybrids would increase the RIE resistance. Polymer 1b-c having smaller mol ratio of methyl α-chloroacrylate had lower EB sensitivity than 1a. The α-chloro group may be attributable to increasing EB sensitivity of 1a-c. Polymer 1d has organo tin group that would potentially contribute to increasing the RIE resistance by the formation of tin oxide.[6] EB sensitivity and RIE resistance of 2/TEOS hybrid having polymethylphenylsilane segment were higher than those of 1a-d/TEOS hybrid, although EB sensitivity of PMPS film was low.[7] It is supposed that the larger mol ratio of the phenyl group increases the RIE resistance and furthermore, the polysilane segment increases the miscibility between organic polymer and silica matrix, resulting in the higher EB sensitivity. Small content of α-chloro group in 2 could potentially be effective to promote the EB induced degradation of the polysilane segment via Si-Si bond cleavage.

Aluminum thin film was easily vacuum-deposited on the positive pattern from 2/TEOS hybrid without any deformation, although similar aluminum-deposition on PMMA gave the rough surface. This contrasting results could be attributable to the higher heat resistance of 2/TEOS hybrid than that of PMMA.

<table>
<thead>
<tr>
<th>Resist</th>
<th>EB Sensitivity / μC cm²</th>
<th>γ-value</th>
<th>RIE selectivity</th>
</tr>
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<tbody>
<tr>
<td>1a</td>
<td>500</td>
<td>0.95</td>
<td>2.92</td>
</tr>
<tr>
<td>1a/TEOS</td>
<td>500</td>
<td>1.50</td>
<td>3.42</td>
</tr>
<tr>
<td>1b</td>
<td>900</td>
<td>0.82</td>
<td></td>
</tr>
<tr>
<td>1c</td>
<td>900</td>
<td>1.12</td>
<td></td>
</tr>
<tr>
<td>1d</td>
<td>500</td>
<td>0.72</td>
<td>3.70</td>
</tr>
<tr>
<td>1d/TEOS</td>
<td>400</td>
<td>0.83</td>
<td>3.65</td>
</tr>
<tr>
<td>1e</td>
<td>600</td>
<td>0.75</td>
<td></td>
</tr>
<tr>
<td>2/TEOS</td>
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<td>1.18</td>
<td>4.45</td>
</tr>
<tr>
<td>PMMA</td>
<td>120</td>
<td>2.00</td>
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</tr>
<tr>
<td>ZEP</td>
<td>80</td>
<td>6.00</td>
<td>3.00</td>
</tr>
<tr>
<td>PMPS</td>
<td>&gt;1000</td>
<td>1.25</td>
<td>5.02</td>
</tr>
</tbody>
</table>

* Relative etching resistance of the resists against quartz glass = 0.68 / etching rate of the resists; etching rate of quartz = 0.68 μm min⁻¹.

Figure 1. Cross-section of the positive pattern from 1a/TEOS hybrid observed by ZYGO (left) and plot of dose and the positive pattern-depth (right).
4. Conclusion
The organic-inorganic hybrid thin films were synthesized and were applied to analogue resists for EB lithography. The EB sensitivity of the hybrid films was almost comparable to that of PMMA. The positive pattern from the hybrids could be transferred to the underlying quartz glass plate by RIE and be coated with metal thin film by its vacuum-deposition owing to the sufficient RIE resistance and heat resistance of the hybrids. These processes would potentially be applied to fabrication of not only optical elements but also silicon chips.

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References