Van der Waals Interaction between Polymer Aggregates and Substrate Surface Analyzed by Atomic Force Microscope (AFM)

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The peeling property of the resist pattern can be analyzed on the point of van der Waals (vdW) interaction between polymer aggregates and substrate by using the atomic force microscope (AFM). By treating the substrate with hexamethyldisilazane (HMDS), the interaction length between tip and substrate is shortened and weakened. It is clarified that a part of polymer aggregates condensed at pattern bottom have no contribution to the interaction with the substrate because the interaction length becomes short. At the resist-substrate interface, a certain vacancy among the polymer aggregates is found out. Based on the aggregation model, it is clarified that exposing the substrate to HMDS vapor acts to weaken the peeling strength of the resist pattern.

Keywords: polymer aggregate, adhesion, peeling, atomic force microscope, surface energy, vacancy, silane-coupling treatment

1. Introduction

The improvement of the adhesion strength of the resist micropattern has been recognized as a serious problem that need to be solved. Furthermore, the condensation control of polymer aggregates in the resist pattern is required for the improvement of line edge roughness (LER) at the resist-substrate interface. In this regard, the present authors have already proposed the novel principle for analyzing resist pattern adhesion and cohesion, that is, DPAT (direct peeling with atomic force microscope (AFM) tip) method. By this method, various properties of micro resist pattern have been clarified. Young's modulus of the dot resist pattern ranging from 84 to 364 nm diameter is determined. Surface depth profile and distribution of hardened layer on resist pattern due to deep UV curing is determined. In a dry condition, the hexamethyldisilazane (HMDS) treatment acts to decrease adhesion strength between a resist and a substrate.

In this study, based on the van der Waals (vdW) interaction, interaction force between the polymer aggregates and the substrate surface which is treated by the HMDS vapor is characterized by using the AFM. By the HMDS treatment, it is clearly observed that the vdW force between polymer aggregates and substrate surface becomes weak and acts in short distance. These interaction analysis prove clearly that the HMDS treatment acts to weaken the adhesion strength between resist and substrate in a dry condition.

2. Experiment

2.1 Sample preparation

A chemically amplified positive resist consisting of polyhydroxystyrene with acid labile blocking groups and photoacid generators was used. The blocking group was tert-butoxy carbonyl (t-BOC). The photoacid generator was trifluoromethanesulfonic acid. Silane-coupling treatment with HMDS was performed prior to spin-coating of the resist film. In order to investigate the influence of silane-coupling treatment on peeling behavior, the Si(100) wafers were exposed to the HMDS vapor for the range of 5-25 s at 90°C on a hot plate. The resist film of 480 nm thickness was coated onto the Si substrates by the spin method. Pre-baking was carried out at 90°C for 60 s. The resist patterns of 130 nm width and 500 nm length were transferred to the resist film using a stepper (Nikon,

NSR, NA = 0.55) with the irradiation energy of 22 mJ/cm². Post exposure baking was accomplished at 90°C for 105s. Subsequently, the resist patterns were developed by dipping into tetramethylammoniumhydroxide (TMAH) 2.38 % aqueous solution for 90s and were subsequently rinsed in the deionized water. Finally, these patterns were dried by the spin method. In order to observe the resist patterns, a scanning electron microscope (SEM; S-4100 made by Hitachi LTD.) was also used.

2.2 VdW interaction measurement

A commercially available AFM, integrated with a microtip (AFM tip), was used for the vdW interaction investigation. As a tip used for the investigation, a conical tip mounted on the cantilever apex was used. The radius of curvature of the tip apex is approximately 8 nm. The tip is made of a Si single crystal. Calibration measurements of the spring constant correlated well with the manufacturer's given value of k = 0.75N/m, which was used in all calculations.

Figure 1 shows a schematic explanation of the vdW interaction between tip apex and substrate.

\[
F = \frac{A R}{6D^2},
\]

where the symbol A represents Hamaker constant. Force measurements were performed using the AFM tip, which surface energy is equivalent to that of polymer aggregate of the resist pattern. The deflection of the cantilever was recorded as a function of piezo movement during approach of the tip. The cantilever displacement, brought out by contacting the resist pattern, was detected using a laser reflection system. The interaction force F is determined by multiplying the measured cantilever displacement by the calibrated spring constant of the cantilever. All investigations were carried out in a dry atmosphere (23°C, 4%RH).

2.3 Pattern peel by the DPAT method

Figure 2 shows the DPAT concept. (a): Prior to the pattern peeling experiment, the resist patterns were imaged in the non-contact mode of the AFM. Subsequently, the tip traversed the resist pattern at the center position upon moving the substrate. (b): By directly applying load to the top corner of the resist pattern with a cantilever tip, the resist pattern
adhering on the substrate can be peeled easily. The pattern peeling can be confirmed by imaging the sample surface in the non-contact mode. Neither the AFM tip nor the silicon substrate appeared to be damaged as a result of the DPAT procedure.

2.3 Surface energy analysis

We have analyzed surface energy of the tip and resist materials using a two-parameter model for interfacial interactions discussed by Kaelble and Fowkes. From this model, the following relationships for surface energy $\gamma$ can be derived based on van der Waal's interaction.

$$\gamma = \gamma^d + \gamma^p,$$

where the superscripts, $d$ and $p$, refer to dispersion (nonpolar) and polar components, respectively. To determine the components of surface energy $\gamma$ of each surface, contact-angle measurement was carried out at 25°C with a goniometer. Using a consistent set of fluids, it is hoped that meaningful relative values will result. The test liquids of which surface energy components, $\gamma^d$ and $\gamma^p$, are known were sessile-dropped. The contact angles of the test liquids were measured within 1 min after making a contact with the surfaces. Table-I summarizes the component of surface energy of test liquids.

<table>
<thead>
<tr>
<th>Test liquids</th>
<th>$\gamma^d$</th>
<th>$\gamma^p$</th>
<th>$\gamma$</th>
</tr>
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<tbody>
<tr>
<td>Deionized water</td>
<td>21.8</td>
<td>51.0</td>
<td>72.8</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>29.4</td>
<td>18.3</td>
<td>47.7</td>
</tr>
<tr>
<td>Diiodomethane</td>
<td>48.3</td>
<td>2.5</td>
<td>50.8</td>
</tr>
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</table>

### 3. Results and Discussion

#### 3.1 Polymer aggregates condensed in resist pattern

Figure 3a shows AFM image of the resist patterns of 130 nm width fabricated on the Si substrate. The aspect ratio of the resist patterns was approximately 3.7. The pattern shape is slightly rounded and the pattern edge with LER due to polymer aggregation can be observed. Figure 3b shows the AFM image of resist residue formed on the substrate after pattern peel investigation. A certain vacancy among polymer aggregates can be clearly observed. Therefore, we can say with fair certainty that the actual contact area at the resist-substrate interface differs from the apparent one, which is estimated by the conventional SEM observation. The vdW interaction between polymer aggregates and substrate can be discussed in the following section.

#### 3.2 VdW force measurement between tip apex and substrate

Prior to interaction investigation, surface property of the tip apex of the AFM is required to be equivalent to that of polymer aggregates. Table-II summarizes surface energy and its component for the tip and the resist materials. In Table-II, it is clear that the polar component $\gamma^p$ of the resist material is lower than that of the dispersion component $\gamma^d$, simply because the polar group density on the resist surface is quite low. Meanwhile, by exposing the Si substrate to HMDS vapor, the polar component $\gamma^p$ of the Si tip material decreases considerably, and surface energy $\gamma$ approaches to that of the resist material. This is because the surface of the Si tip becomes hydrophobic, terminated with trimethylsylil groups, on the other hand, the surface without exposing to the HMDS vapor was hydrophilic, covered with a native oxide layer. No change of dispersion component $\gamma^d$ of the Si tip is clearly observed. Therefore, judging from the above discussion, we can say with fair certainty that the surface nature of the Si tip with the HMDS treatment is equivalent to the polymer aggregates.

<table>
<thead>
<tr>
<th>Materials</th>
<th>$\gamma^d$</th>
<th>$\gamma^p$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si(100)</td>
<td>18.2</td>
<td>50.4</td>
<td>68.6</td>
</tr>
<tr>
<td>Si(100) with HMDS</td>
<td>21.1</td>
<td>20.5</td>
<td>41.6</td>
</tr>
<tr>
<td>Resist</td>
<td>29.6</td>
<td>12.8</td>
<td>42.4</td>
</tr>
</tbody>
</table>

#### 3.3 Interaction measurement between tip and substrate

Figure 4 shows the force-distance curve between tip and substrate. Hence, the interaction length is defined as the distance at which the interaction force begins to acts between tip and substrate. By treating the Si substrate with HMDS vapor, the interaction becomes weak and acts in
short distance. Therefore, in this way, the slight change of surface nature of the solid surface can be detected by using the AFM tip. One can safely state that the exposure of the substrate to the HMDS vapor acts to weaken the adhesion strength between tip and substrate in a dry condition.

3.4 Interaction model between polymer aggregates and substrate.

Based on the experimental data, the interaction model between polymer aggregates and substrate surface can be constructed, and the correlation with the peeling behavior is discussed as mentioned later. Line edge roughness due to condensation of polymer aggregates has been recognized as a serious problem that need to be solved. However, as shown in Fig.5, it is entirely fair to say that condensation of polymer aggregates affects to the interface property between resist pattern and substrate such as pattern collapse.

Let us now attempt to extend the observation into interfacial region. Figure 6 shows the schematic of enlarged cross section model of the resist-substrate interface. Several polymer aggregates, A–D are condensed and interacted to the substrate surface. Some vacancy can be illustrated at the interface region. In this case, for the simplified discussion, diameter of all polymer aggregate is same. As shown in Fig.6, in each polymer aggregate, the interaction length between the aggregate and the substrate surface is different. Moreover, interaction length can be changed by the HMDS treatment, as follows. The dashed line, a–a', represents the interaction length between the polymer aggregate and the substrate surface with no surface treatment. On the other hand, the dashed line, b–b', is approached the substrate surface compared with the line a–a'. Dashed line, b–b', represents the interaction length between the polymer aggregate and the substrate surface on which HMDS treatment is performed. Therefore, in the case of the dashed line (a–a'), most of polymer aggregates contribute to interaction with substrate surface. However, by the HMDS treatment, polymer aggregates (C and D) have no contribution to the interaction with the substrate surface because the interaction length becomes short (b–b'). By the HMDS treatment of the substrate surface, we can be fairly certain that the peeling strength of resist pattern adhered on the substrate becomes weak. In the following section, the peeling strength of resist pattern is analyzed experimentally by the DPAT method.

3.5 Pattern peeling by DPAT method

Figure 7 shows the AFM images of pattern peel investigation. By applying a certain load with the
AFM tip (white arrow), the resist pattern can be peeled easily. Figure 8 shows the experimental result with regard to the pattern peel property for these differently exposing time to the HMDS vapor. When the exposing time to the HMDS vapor is zero, no pattern remains on the Si substrate after the pattern development because of the liquid intrusion into the resist-substrate interface due to hydrophilic nature of the substrate. As shown in Fig.8, the load for pattern peeling $F_p$ decreases and approaches to the amount of $1.5 \mu N$ as the exposing time to the HMDS vapor increases. The load is slightly deviated, but still is well within the range of experimental scatter. Therefore, in a dry atmosphere, one can confidently state that the silane-coupling treatment has an effect to decrease the peeling strength of the resist pattern to the Si substrate. These results are consistent with the vDW interaction investigation by using the AFM.

4. Conclusion

The peeling property of the resist pattern can be analyzed on the point of vDW interaction of polymer aggregates by the DPAT method. The followings were obtained as the major conclusions.

(i): At the resist-substrate interface, a certain vacancy exists among the polymer aggregates.
(ii): By treating the AFM tip with HMDS vapor, surface energy of the tip can be controlled to be equivalent to that of resist material.
(iii): Due to the vDW interaction measurement with the AFM tip, the interaction length between tip and substrate is shortened and weakened by the HMDS treatment of the substrate.
(iv): A part of polymer aggregates condensed at pattern bottom have no contribution to the interaction with the substrate surface because the interaction length becomes short.
(v): Exposing the substrate to the HMDS vapor acts to weaken the peeling strength of the resist pattern from the substrate.

Understanding the peeling property of resist pattern based on the condensation of the polymer aggregates is of crucial importance for development not only microelectronic devices but quantum devices in nanometer scale. This technique will prove useful in other fields, for example, for the condensation control of microparticles and the structural design of micro- and nanomachines and so on.

Acknowledgement

This work was partially supported by the Grant-in-Aid for Scientific Research (C) of the Ministry of Education, Science, Sports and Culture. (No.13650373). Part of this work was also performed under the Research Foundation For Material Science and HOSOKAWA POWDER TECHNOLOGY FOUNDATION..

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