Vertical Density Profiles of Various Photoresists and Top-coats by X-ray Reflectivity Analysis

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Vertical electron density profiles of various photoresist, top-coat and their combinations as bilayers were obtained from X-ray reflectivity analysis. The result suggests that there are specific layers with different electron density near the surface of photoresists and top-coat films. The investigation on bilayer films which consist of photoresist and top-coat shows that the intermixing of two materials and the roughness of films are varied by annealing (baking) time and temperature.

Keyword: immersion lithography, photoresist, top-coat, X-ray reflectivity

1. Introduction

With the minimization of the device size, the pattern density for the given area has increased and the pattern size itself has tremendously decreased down to the 50nm for the mass production in these days. For the patterning of sub 50nm, the ArF(193nm) immersion lithography has been widely accepted as a standard method to make this dimension without critical problems[1]. The basic idea of immersion lithography is to fill the space between the final lens element and the photoresist with a fluid which has a much higher refractive index than air so that the resolution and the depth of focus can be enhanced[2]. Water is widely used as a medium fluid for commercialized immersion scanners and the resolution reached out about sub 40nm.

At the first stage of water immersion lithography, there are a lot of problems since water is directly contacted with photoresist as well as lens element. Pattern degradation and lens contamination were occurred by the leaching of PAG molecule in photoresist to water media. To prevent this leaching problem efficiently, topcoat material was developed and successfully introduced in immersion lithography to solve lithographic defect issue as well as lens contamination problem. The main role of topcoat material is to prevent photoresist component from leaching to water. Nowadays most device makers adapted the topcoat process as a basic process for water immersion lithography and are preparing for mass production. Additionally, there is lots of trying to remove top coat material for saving process costs. This kind of resist is usually called as a top coatless photoresist whose included hydrophobic additive which acts as internal top coat materials.

In this whole technical situation, the surface properties and the physical properties of lithographic material determine the defect performance as well as resolution for patterning performance. In spite of this importance of understanding physical properties, there has been...
little investigation regarding direct analysis of photoresists as well as top coat material. It is very difficult to analyze these materials since top coat materials and photoresists are composed of several different components.

In this study, analyzing method (X-ray reflectivity analysis) for the physical properties of top coats and photoresist will be suggested and applied to understand several commercialized products. The main interest is vertical electron density profiles of films which are depending on the process variables such as time and temperature and the interfacial behavior of bilayer system when topcoat and photoresist coated sequentially.

1. Experiments

2.1 Sample preparation

Several kinds of commercial photoresists based on acrylate polymer resin and top-coats (TC) based on fluorinated polymer for immersion lithography were supplied from various material makers.

All the polymers for instrumental analysis were spin-coated on clean Si wafers (100) at the speed of 1500 rpm for 60s. To study the physical phenomena near interface, the six combinations of three normal photoresists and two top-coats for immersion process were made into bilayer thin films. First, the photoresists were coated on Si wafer and the top-coats did right after that.

Each thin film was thermally treated in various conditions. Each normal photoresist and top-coat was baked at two different temperatures (100°C and 150°C) for 2 min. These two different conditions were set up for the preparations to investigate the bilayer films. Bilayer films were treated at four different conditions. Each combination of photoresist and top-coat was annealed at 100°C and 150°C for 2 min and 35 hour. These annealing conditions could figure out the effects of temperature and annealing time on the physical properties of photoresist, top-coat and even the combinations of them.

2.2 X-ray Reflectivity Analysis

X-ray reflectivity analysis is a powerful, nondestructive method for structural characterization of thin films and multi-layered structure[3,4]. When the X-ray wave is incident upon a surface of film at sufficiently low angle, it is reflected, absorbed, or scattered. A detector which is at the same angle, but opposite side of incident beam can collect beam scattered and reflected, and that makes the reflectivity oscillation which contains the information about the thickness, roughness, and even electron densities[5]. To investigate the density profile along the normal direction to surface, this X-ray reflectivity analysis including fitting process for electron density profile was used.

All the thin films except the model photoresist were tested in 10C1 beam line at PAL (Pohang Accelerator Laboratory) with 2.5GeV beam source. A wavelength of X-ray beam was 1.54Å and all measurement was taken for less than 5 min. Usually, it takes more than 20 min to measure one sample with a standard procedure, but the amount of beam dose was reduced by compulsion to minimize the damage of chemical structures inside photoresists, though the background noise slightly increased. Many kinds of fitting algorithms and programs exist, but Parratt 32 (ver. 1.6), most traditional system was selected since the films are relatively thick (more that 100nm) and even get a multi-layer structure. Through the fitting process with Parratt 32, several possible models describing the structures of films were tested and fitted, and then the final result was selected. Those models contain the thickness, electron density, and roughness (or diffusivity at interface) of each layers.
2. Results and discussions

3.1 Electron density profile inside each film

Figure 1 shows the electron density profiles inside normal photoresists which were calculated from fitting X-ray reflectivity curves with 2 or 3 layer models. Commonly, the thickness of films baked at high temperature is slightly thinner than that baked at low temperature. Also, the electron densities which are proportion to density of film show same tendency with thickness of film. From these result, we can conclude that the some part of film like residual solvents are got rid of more at high baking temperature since the integrals of polymer part in Figure 1 are reduced.

On the other hand, all of the result insists that there are high density layer near the top of the surface. At first, 1 layer model was tried to fit reflectivity data, but every calculation was converged to unrealistic, wrong answers. Therefore, more layers were introduced to the top or bottom of the 1 layer model, the data were re-fitted, and finally the result in Figure 1 was drawn out. The formation of high density layer seems to result from the factors extrinsic to the chemical structures of photoresist resin, since all of photoresist shows high density region in spite of different chemical structures. In fact, photoresists are not a single-component system, so they contain some other parts such as PAG, quencher, or other molecules. Those high density layers are seemed to be generated by moving those components out to the surface to stabilize surface energy[6]. In addition to that, it seems that the baking step and its condition are not critically important to the generation of these layers.

Electron density profiles for TCA and TCB are quit different (Figure 2). TCA is much thinner than TCB, and the appearances of profiles are also different. Especially, fitting the reflectivity curves of TCB was not enough with 2 or 3-layer models, so 5-layer model was used for fitting process. The diffusivity of TCB is larger than that of TCB and even that of photoresists. This characteristic continues on the bilayer of photoresist and top-coat.

Figure 1. Electron density profiles of normal photoresists. Each figure shows the thickness (in nm scale) and the diffusivity ($\sigma$ in Å, similar to roughness) both numerically and graphically.
3.3 Physical changes on the interface during thermal treatments

Thermal treatment on the photoresist and top-coat influences on the physical properties of thin film[7]. These effects on the film can be the direct or indirect cause of defects on patterns. Especially, when the several kinds of polymers such as photoresist, top-coat, and ARC (Anti-Reflection Coating) adjoin to each other, even a short bake process can make physical changes like the intermixing of two components. In fact, the top of the photoresist can be washed out unintentionally with top-coat during the developing process of top-coat. That can make the roundness of top of the patterns, even serious defects. In this research, the inner structures near interface of two different polymer components were investigated by X-ray reflectivity analysis. In addition, the effect of the temperature and time duration of thermal treatment on the bilayer film composed photoresist and top-coat was studied.

First, from the results in Table 2, rising baking temperature and annealing the samples for long time reduce the thickness of film and also the diffusivities between each layer. Of course, it is a matter of degree, the decrement of diffusivities and thickness of each layer is still common to all results. After the spin-coating, the film has an inherent stress and a lot of vacancies due to fast solvent evaporation. During the annealing the samples at high temperature, these potential facts for changes make an effort to regain energy equilibrium. High temperature, in other words, high energy is the key to make the changes of chain conformation, therefore the thickness of film more easily decrease when the film is baked at high temperature for long time.

Second, some of these six combinations of photoresist and top-coat have different characteristics of reaction to different annealing conditions. Some show more dramatic changes in the appearance of reflectivity curves as the temperature is varied, while the others are more sensitive to the annealing time duration. For example, in

<table>
<thead>
<tr>
<th>Diffusivities of interface &amp; roughness of surface</th>
<th>100°C 2min</th>
<th>150°C 2min</th>
<th>100°C 35hours</th>
<th>150°C 35hours</th>
</tr>
</thead>
<tbody>
<tr>
<td>PRA +TCA</td>
<td>△</td>
<td>○</td>
<td>△</td>
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</tr>
<tr>
<td>PRB +TCA</td>
<td>△</td>
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<tr>
<td>PRC +TCA</td>
<td>○</td>
<td>○</td>
<td>△</td>
<td>○</td>
</tr>
<tr>
<td>PRA +TCB</td>
<td>△</td>
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<td>×</td>
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<tr>
<td>PRB +TCB</td>
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<td>PRC +TCB</td>
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Table 2, the bilayer film of PRA and TCA is barely changed as the temperature is varied without reference to annealing time, but the time affects the inner structures of film apparently. On the other hand, the bilayer film of PRB and TCB is more sensitive to time duration. There is not a noticeable change on the amplitude of two reflectivity curve: 100°C 2min and 150°C 2min. Enough time, however, give a chance to recover the smoothness of interface to this bilayer sample, and the noticeable changes of amplitude can be found in the sample with the enough annealing time duration.

3.4 Electron density profiles of TCA on PRB

One of the reflectivity curves of the combination, TCA on PRB was simulated and fitted. Figure 4 shows the electron density profiles of PRB and TCA bilayer from various annealing.

![Figure 4](image)

Figure 4. Electron density profiles of PRB and TCA bilayer from various annealing. Black and red profiles mean that the films annealed in 100°C and 150°C for 2 min each, and blue profile stands for the film annealed in 150°C for 35 hours.

Black line in Figure 4 shows the electron density profile described by 5 layer model. Only in case of black profile, some parts of reflectivity curve couldn’t resemble the real one more, in other words, fitting software could not develop the model further. It seems that there might be unexpected physical phenomena such as diffused reflection, or geometrical inhomogeneity at the interface. Other PRB+TCA films with other annealing condition are relatively fitted well by the model with a fewer layers, and that also support the instability at the interface.

In case of red and blue profiles in Figure 4, anyway, one can find that the diffusivity at interface is getting diffuser and the thickness of PRA decrease drastically as the annealing proceeds. Also, the density of film increase and thickness of film decrease when the film is annealed.

3. Conclusions

From the X-ray reflectivity analysis of various photoresists, high density layers at the top of the photoresist films were discovered. It was supposed that the formation of high density layers is due to the surface enrichment of additives to have low surface energy of the system. Secondly, the bilayer films of photoresist and top-coats have a different thermal characteristic: The sensitivity to annealing temperature or time duration. In fact, the combination of PRB and TCB shows improvement on diffusivity of interface and surface roughness as the annealing time increase, while the combination of PRA and TCA is more affected by annealing temperature. One of the reflectivity results of those combination was analyzed using the fitting technique, and the instability at the interface between the photoresist and top-coat was suggested when the sample was baked at a low temperature for short time.

Acknowledgements

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