Understanding Ultra-Thin Film Resist and Underlayer Performance through Physical Characterization

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The physical characterization of extreme ultraviolet (EUV) ultra-thin underlayers (ULs) and their effects on photoresist EUV lithographic performance was investigated. UL polymer compositions were modeled to identify polymer compositions that would encompass a range of glass transition temperatures (Tg) and surface polarities. Eight UL polymers compositions were synthesized and characterized, demonstrating that polymer composition can dictate the surface polarity and Tg properties of cross-linked UL films. The Tg of UL films drops significantly for film thicknesses below ~30 nm. EUV imaging of open source and commercial resists on the eight UL films was evaluated. Resist adhesion improved when the surface polarity of the underlayers decreased. It was discovered that the coefficient of thermal expansion (CTE) plays an important role in determining the adhesion of resist to underlayers.

Keywords: EUVL, ARC, underlayer properties, resist adhesion

1. Introduction

Extreme ultraviolet (EUV) lithography is expected to offer a single-exposure solution for 22 nm half pitch imaging. However, to successfully implement EUV lithography, further understanding of the lithographic performance of EUV photoresist is needed. Critical to the successful implementation of I-line, deep ultraviolet (DUV), and 193 nm resist technologies was the development of antireflective coatings (ARCs). In EUV lithography, however, the initial conclusion was that ARCs were not required because the reflectivity of silicon surfaces at 13.5 nm was very low. Nonetheless, combining DUV ARCs with EUV resists has been shown to improve lithographic imaging [1-3]. Although some explanations have been advanced to explain the reasons for the improved lithographic performance, the fundamental principles behind understanding the experimental results have not yet been proposed. In particular, there are many fundamental problems and interactions between thin resist films and thin underlayer films that are not well understood, especially with a lack of disclosure of material composition and greatly differing imaging responses.

Here we present our work on furthering the understanding of EUV underlayer physical properties and their impact on resist performance. We have developed a set of eight simple polymer films and formulated them into EUV underlayer compositions without antireflective properties to study the fundamental interactions between ultra-thin underlayer and resist films. The thermal properties (glass transition temperature and coefficient of thermal expansion) and surface properties (polarity and H2O contact angle) of the resulting underlayer thin films were evaluated and compared with their ability to support EUV imaging. We investigated the lithographic impact of the underlayers on our...
open source resist (OS2) [4] and a commercially available resist (Resist B).

2. Experimental
2.1 Underlayer polymer design
Our strategy for designing various underlayer polymers was to develop a simple model for predicting the glass transition temperature (Tg) and surface polarity of each underlayer that we intended to prepare. The Tg of the underlayer polymers was predicted using the Fox Tg method [5]. The surface polarity of the underlayer polymers was modeled from the Hanson solubility terms of each monomer [6] by combining these values according to the mole fraction of each monomer in the polymer. The monomers examined in this study are shown in Fig. 1. Various polymer combinations were modeled by varying monomer type, number of different monomers, and mole fraction. All polymers contained at least 5 mol% of the cross-linkable monomer hydroxyethyl methacrylate (HEMA).

![Diagram](https://via.placeholder.com/150)

Fig 1. Underlayer materials and general experimental scheme used in this study.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>HEMA</th>
<th>BA</th>
<th>Sty</th>
<th>BrSty</th>
<th>MMA</th>
<th>Predicted Fox Tg ºC</th>
<th>Predicted Polarity</th>
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<tr>
<td>UL2</td>
<td>20</td>
<td>10</td>
<td>0</td>
<td>0</td>
<td>70</td>
<td>70</td>
<td>5.8</td>
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<tr>
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<td>5</td>
<td>10</td>
<td>20</td>
<td>20</td>
<td>45</td>
<td>92</td>
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<tr>
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<td>30</td>
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<td>6.3</td>
</tr>
<tr>
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<td>15</td>
<td>19</td>
<td>10</td>
<td>0</td>
<td>56</td>
<td>49</td>
<td>5.0</td>
</tr>
<tr>
<td>UL6</td>
<td>17</td>
<td>51</td>
<td>32</td>
<td>0</td>
<td>0</td>
<td>-7</td>
<td>3.8</td>
</tr>
<tr>
<td>UL7</td>
<td>45</td>
<td>49</td>
<td>0</td>
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<td>-7</td>
<td>6.2</td>
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<tr>
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<td>32</td>
<td>16</td>
<td>0</td>
<td>0</td>
<td>52</td>
<td>50</td>
<td>6.2</td>
</tr>
<tr>
<td>UL9</td>
<td>7</td>
<td>22</td>
<td>25</td>
<td>7</td>
<td>39</td>
<td>51</td>
<td>3.9</td>
</tr>
</tbody>
</table>

Table 1. Underlayer polymer compositions synthesized and their predicted polymer Tg and surface polarity parameters.
the fractional thickness change per degree change, for these polymers above and below the Tg.

2.4 Surface polarity
The surface free energy polarity of each underlayer was determined using the method developed by Owens and Wendt [7]. In this method, contact angles formed between various solvents and a solid film can be plotted along with the known dispersion and polar surface energies of the solvents using equation 1, which is of the form

\[ y = mx + b, \]

where \( \theta \) is the contact angle formed, \( \gamma_i^d \) is the dispersion surface free energy of the test liquid, \( \gamma_i^p \) is the polar surface free energy of the test liquid, \( \gamma_f^d \) is the dispersion free energy of the polymer film, and \( \gamma_f^p \) is the polar free energy of the solid. The surface free energy polarity of the polymer film can be determined from the slope of the plot.

\[ (1 + \cos \theta) \frac{\gamma_f}{2(\gamma_f^d)^{1/2}} = (\gamma_f^d)^{1/2} + (\gamma_f^p)^{1/2}\left(\frac{\gamma_f^p}{\gamma_f^d}\right)^{1/2} \]

For this study, the contact angle of each polymer was measured using four different liquids of varying dispersion (26.2-48.3 mN/m) and polar (2.5-46.5 mN/m) surface energies. The test liquids studied consisted of water, formamide, dimethyl sulfoxide and diiodomethane.

Resist surface polarity was qualitatively determined by using only the water contact angle as the other solvents were found to dissolve the resist during measurement. Underlayer experiments, however, showed a strong correlation between smaller water contact angles and larger surface polarity, and thus water serves as a good indication of the polymer surface polarity.

2.5 Photoresist materials and process
We evaluated resist imaging on underlayers using our OS2 resist formulation composed of 15 wt% of solids of Di(4-tert-butylphenyl) iodonium perfluoro-1-butane-sulfonate (DBTPI-PFBS) photoacid generator (PAG), 1.5 wt% of solids of tetrabutylammonium hydroxide base (TBAH), 4-hydroxystyrene/styrene/t-butyl acrylate (65/15/20) polymer, and a 50/50 mixture of ethyl lactate and propylene glycol methyl ether acetate (PGMEA) [26] and the commercial resist. Resist B. Underlayer samples were coated to a thickness of 30 nm. Resist were then spin-coated and soft-baked to a film thickness of 60 nm on top of the underlayer. Soft-bake temperatures for OS2 and Resist B were 130 °C/60 s and 110 °C/90 s, respectively. Exposures were performed using dense line/space patterns on the Berkeley EUV microexposure tool (MET), followed by post-exposure bake (PEB) and 45s development in 0.26N Me2N′OH. The conditions for OS2 and Resist B were 120 °C/90 s and 100 °C/60 s, respectively.

3. Results and Discussion
3.1 Glass transition temperatures of EUV underlayers.
Eight acrylic polymers were formulated into sixteen underlayer films using 6 and 12 wt% cross-linker. Figure 2 shows the measured Tg of the underlayer films, which ranged from ~40-100 °C and were typically larger than predicted by the Fox Tg. The Fox Tg, however, does not account for possible differences due to cross-linking or small blended molecules such as TAG or free cross-linkers. Surprisingly, the films show little change in Tg when the level of cross-linker increases from 6-12 wt% of solids. This result was surprising as we expected both the degree of cross-linking and possible excess cross-linker (which may act as a plasticizer) to have a greater effect on the Tg of the underlayer films.

![Fig. 2. Tg of UL films containing different polymer compositions at two different cross-linker loadings as determined by ellipsometry vs. predicted Fox Tg.](image-url)
3.2 Glass transition temperature of underlayer through thickness

Three underlayer polymers (UL2, UL3, UL4) were selected for a detailed study of the effect of film thickness on Tg. The three underlayers prepared from these polymers exhibit a range of Tgs at 30 nm film thickness (~85, 100 and 60 °C) and have a broad range of HEMA monomer (20, 5 and 30 mol%). Initially, UL2 was examined at various film thicknesses using both spectroscopic ellipsometry and X-ray reflectometry. Figure 3a compares the Tg of UL2 at various film thicknesses obtained by both ellipsometry and XR². Both techniques show similar UL2 Tg values as well as an eventual decrease in Tg with thinner films. They do differ slightly, however, in the critical thickness at which Tg starts to decrease. This could be due to differences in the rate of change in temperature during Tg measurements. The thermal ramp rate used by XR² is an order of magnitude slower than that used by ellipsometry. The slower ramp rate could explain the lower Tgs determined by XR², particularly in thinner films. Figure 3b compares the glass transition temperatures of UL2, UL3 and UL4 obtained using ellipsometry. Despite distinct differences in composition, all three underlayers show a consistent Tg when the films are 30-200 nm thick, but all show similar decreases in Tg when film thicknesses drop below 30 nm. Other researchers have also observed such changes in Tg for polymer materials through thickness [8-29] and some have suggested that a decreases in Tg in ultra-thin films indicate weak interactions between the polymer and substrate [15,29].

3.3 Surface polarity of EUV underlayers

The surface energies of each underlayer polymer composition were measured using 6 and 12 wt% cross-linker, as described previously. Figure 4a shows the Owens-Wendt plots for all eight underlayers. A high degree of linearity was obtained for all underlayers, and the varying response in surface polarity can be easily inferred from the slopes of the plots. A range of underlayer surface polarities (1.6-3.6 mN/m) was determined as designed (Fig. 4b). The surface polarity of the underlayers, however, was found to be independent of cross-linker level. This result is surprising as we expected changes in cross-linker level to change the amount of hydroxyl groups at the underlayer surface and thus change the surface polarity of the film.

3.4 EUV underlayer imaging effects

Lithographic imaging was performed for 60 nm thick films of OS2 and Resist B on all underlayers to ascertain the effects of varying underlayer thermal and surface properties on imaging. The scanning electron microscope (SEM) images and line edge roughness (LER) results of 40 nm dense lines for OS2 on UL’s 2-9 (compositions described in table 1) formulated with 12 wt% cross-linker are shown as a function
of UL Tg and water contact angle for OS2 (Fig. 5) and Resist B (Fig. 6). Both OS2 and Resist B show varying responses in LER and adhesion based on the underlayer tested.

The most interesting result of this three-dimensional map of imaging as a function of underlayer polarity and Tg is the effect of surface polarity (H₂O contact angle). It appears that the adhesion is worse at intermediate polarities. Our expectation was that adhesion to the underlayers would parallel what is generally know about HMDS-priming of silicon surfaces in that higher contact angles can give better adhesion. The adhesion of UL4, on the other hand, is surprisingly good for both OS2 and Resist B despite its low H₂O contact angle.

To a lesser degree, the Tg of the underlayer appears to play a role. The adhesion of both resists is worse on UL7, which has the lowest Tg. UL2 and UL8 have roughly the same water contact angles as UL7, but higher Tgs and slightly better adhesion to both resists.

Fig. 4. A) Owens-Wendt plot for underlayers UL2-9 B) Plot of surface free energy vs. underlayers

Fig. 5. OS2 resist LER and adhesion as a function of underlayer Tg and water contact angle.
3.4.1 Underlayer surface polarity and compositional effects on resist adhesion

Figures 7-8 use a semi-quantitative measure of resist adhesion based on the size of the lines (resolution) at which adhesion fails. The resolution reported is the width of the smallest dense lines exhibiting pattern collapse or delineation. Figure 7 shows the line size at which adhesion fails for OS2 and Resist B as a function of a) surface polarity and b) mole% HEMA composition for 30 nm underlayer films. Adhesion improves with decreasing surface polarity and decreasing HEMA content, although OS2 shows a stronger correlation than does Resist B. First, this suggests that the increase in underlayer polarity, driven primarily by the amount of HEMA monomer in the UL polymer, has an adverse effect on resist adhesion at this relatively low cross-linker loading. Second, the less polar OS2 resist appears to be more affected by the change in underlayer surface polarity or [HEMA] than does the more polar Resist B. OS2 and Resist B were found to have a water contact angle of 74° and 66°, respectively.

Figure 8 compares the adhesion failure with the underlayer HEMA composition at 6 and 12 wt% cross-linker levels for a) OS1 and b) Resist B. Interestingly, the data shows significantly improved resist adhesion at 12 wt% cross-linker when compared to 6 wt% cross-linker. Furthermore, the improved resist adhesion at 12 wt% cross-linker more strongly correlates to less surface polarity and lower polymer HEMA compositions. Note that UL4 (circled in Fig 7 and 8) consistently gives good adhesion independent of the surface polarity and [HEMA] explored in these studies.

3.4.2 Underlayer coefficient of thermal expansion

A useful material property that is obtained during Tg measurement is the linear coefficient of thermal expansion (CTE). While measuring the Tg of the various underlayer films, it became apparent that underlayer UL4 was exhibiting a low CTE both below and above its Tg. Figure 9a compares a typical glass transition temperature curve for UL4 and UL9. The slopes of the curves are
Fig. 7. Resolution at which adhesion failure occurs is depicted as a function of underlayer A) surface polarity and B) HEMA concentration for OS2 resist (blue triangle) and Resist B (red circle).

representative of the CTE, clearly showing UL4’s lower CTE in both the glass and melt regimes. The CTEs of all underlayers were therefore investigated (Fig. 9b), demonstrating that UL4 had a significantly lower CTE than all other underlayers investigated.

As noted in section 3.4.1, UL4 promoted resist adhesion despite a high surface polarity. The CTE of UL4 is the only underlayer with a CTE similar to that of the two photoreisists tested. A possible explanation for UL4’s low CTE is that it was the only copolymer that was tested in this study. In addition, UL4 was also the only polymer investigated that contained only methacrylate monomers. These characteristics may lead to better film packing for UL4 and will be investigated in future experiments.

Figure 10 shows a three-dimensional mapping of resist adhesion as a function of both underlayer HEMA composition and CTE. For both a) OS2 and b) Resist B, resist adhesion was improved at both lower [HEMA] and lower CTE. The overall resist adhesion trends in these plots suggest that both underlayer thin film surface polarity and CTE can play a major role in photoreisist adhesion.
3. Conclusions

Eight acryl polymers were synthesized and formulated into EUV underlayer compositions. The thermal and surface properties of the resulting underlayer thin films were evaluated and compared with their ability to support the EUV imaging of our open source resist (OS2) and a commercially available resist (Resist B). We found that the polymer composition can be specifically tailored to give a range of Tg, CTE, and surface polarity properties in the underlayer thin films.

A study of the surface polarity of the underlayer thin films using contact angle found that lower surface polarity generally caused better adhesion with the resists tested in this study. The less polar OS2 showed a stronger adhesion dependency on underlayer surface polarity than the more polar Resist B.

We studied the effect of underlayer thin film Tg as well, finding no clear impact of this thermal property on lithographic imaging. During the course of characterizing underlayer Tg, however, it was found that UL4 had a significantly lower coefficient of thermal expansion (CTE) than the other underlayer thin films investigated. The CTE of underlayer UL4 is similar to those determined for the resists. Underlayer UL4 was found to promote excellent resist adhesion for both resists despite having one of the highest surface polarities. Additional analysis of the other films suggests that a lower underlayer CTE can improve resist

Fig. 9. A) Typical Tg curve depicting the CTE for glassy and melt regions of UL4 and UL9. B) Glass and melt region CTE for all underlayer and resist films investigated in this study.

Fig. 10. Three-dimensional map depicting resolution at which resist adhesion failure occurs in response to changes in underlayer HEMA monomer composition and CTE for A) OS2 resist and B) Resist B.
adhesion when the underlayers have similar surface polarities.

An investigation of the effect of cross-linker levels in the underlayer films found that increasing the level of cross-linker improved resist adhesion without significantly impacting the Tg or surface energy of the film.

We conclude that underlayer CTE, surface polarity, and cross-linker loading can greatly affect ultra-thin film underlayer and resist interactions as seen through variations in resist adhesion and imaging performance. These results give insight into the adhesion mechanisms of ultra-thin EUV resist films on underlayers and allow for further explorations into underlayer thermal and surface property impacts on EUV resist imaging performance.

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