EUV Resist Materials for 16 nm And below Half Pitch Applications

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A series of polymer with different hydrophobicity have been synthesized to investigate effects of contact angle on ultimate resolution. Contact angle of these polymers was widely changed by utilizing polymers having a different chemical structure and protection ratio. It is revealed that resolution of 20 nm half-pitch (hp) was limited by pattern collapse and improved by increasing contact angle of polymer under E-beam exposure. It is noteworthy that resolution of 20 nm hp and below for current EUV resists with exposures on a NXE:3100 and a micro-field exposure tool (MET) at SEMATECH Berkeley was also limited by pattern collapse. Low diffusion character of current EUV resists with controlled PAG design, especially polymer bound PAG (PBP), suppressed degradation of resolution by chemical blur. Combination of high contact angle polymer with low diffusivity PAG showed resolution of 16 nm hp using a MET at SEMATECH Berkeley with a LWR of 3.0 nm, sensitivity of 24 mJ/cm², and Z-factor of 4×10^{-9} mJ·nm³. Unfortunately density of blob defect for the hydrophobic polymer was above 100 counts/cm². Hydrophobicity of film surface was found to be a main cause of its poor defectivity. Adding the new EUV additive to the hydrophobic resist reduced density of blob defect from 100 counts/cm² to below 0.1 counts/cm².

Keywords: EUV lithography, chemically amplified resist material, pattern collapse, resolution, EUV additive

1. Introduction

EUV lithography is one of the most promising candidates for half-pitch (hp) 16 nm node device manufacturing and below. The main issue for developing EUV resist is to satisfy the ITRS target of resolution, line-width roughness (LWR), and sensitivity simultaneously[1-4]. Although 15 nm hp resolution has been recently demonstrated using non CAR on micro-field exposure tool (MET) at SEMATECH Berkeley, its sensitivity of 70 mJ/cm² was still far from target of 15 mJ/cm²[5].

Chemically amplified resist (CAR) serves as a key technology for photolithography of 20 nm hp patterning and below because of its high sensitivity and resolution[6]. We have investigated that resist

blur of CAR is comparable with that of non CAR if we utilize PAG with controlled design, especially polymer bound PAG (PBP)[7,8]. Recent studies have been also revealed that CAR enables resolution capability down to 18 nm by decreasing thickness of resist film even though sensitivity is still high, 40 mJ/cm², for satisfying manufacturing requirement.

We have previously reported that pattern collapse is a limiting factor for resolving the pattern below 20 nm[8]. It is well known that pattern collapse is improved by decreasing capillary force[10]. Although many researchers have investigated effects of processing conditions such as film thickness and rinse materials on decreasing capillary force[11-12], detailed

understanding is still lacking from a perspective of hydrophobicity of resist film.

The present study aims to clarify how large hydrophobicity of resist affects pattern collapse at hp below 16 nm. Accordingly, we synthesized a series of polymers in which their hydrophobicity was changed by utilizing polymers having a different chemical structure and protection ratio. We also report herein EUV performances of such a hydrophobic resist including ultimate resolution, sensitivity, LWR, EL and depth of focus (DOF) using a MET at SEMATECH Berkeley and NXE:3100 at IMEC.

2. Experimental

2.1. Materials

Three series of protected co-polymers were synthesized according to the conventional methods and listed in Table 1. An organic solution containing each of polymer, PAG and organic amine as a quencher was prepared, and the resulting solution was filtered with 0.03 μm polyethylene filter for lithographic evaluation.

Table 1. Protection ratio and contact angle against water for series of polymer with different protection groups.

Polymer	Relative protection ratio	Normalized contact angle
Polymer-A	1.1 ~ 1.9	15 ~ 20°
Polymer-B	1.1 ~ 3.4	1 ~ 16°
Polymer-C	1.5 ~ 2.3	-3 ~ 7°

2.2. Lithographic evaluation using E-beam

The resist solution was filtered and spin-coated on silicon wafer that was treated with a hexamethyldisilazane (HMDS), and pre-baked at 100 °C for 90 sec to give a film thickness of 40 nm. The wafer was exposed with electron beam using a Ushio SOTO1 ($V_{\text{acc}} = 57 \text{ keV}$). After the exposure, the wafer was baked (PEB) at 90 °C for 90 sec or 70 °C for 90 sec, and developed with an 2.38% aqueous trimethylammonium hydroxide (TMAH) solution at 23 °C for 30 sec. The resulting wafer was analyzed by Hitachi S-9380 II CD-SEM tool and Hitachi S-4800 X-SEM tool.

2.3. Lithographic evaluation using EUV light

The resist solution was filtered and spin-coated on silicon wafer that was treated with a HMDS, and pre-baked at 100 °C for 90 sec to give a film thickness of 40 nm. The wafer was exposed with EUV light using a Exitech MET with 0.30 NA and pseudo-PSM dipole illumination at Berkeley. After the exposure, the wafer was baked (PEB) at 70 °C

for 90 sec, and developed with an 2.38 % TMAH solution at 23 °C for 30 sec. The exposed wafer was analyzed by Hitachi S-9380 II CD-SEM tool and Hitachi S-4800 X-SEM tool. Wafers similar to those described above were prepared using a ASML NXE:3100 with 0.25 NA and dipole 60X illumination ($\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.83 / 0.41$) at IMEC.

2.4. Contact angle measurement

To determine hydrophobicity of resist film quantitatively, contact angle of resist film was measured. The resist solution was filtered and spin-coated on silicon wafer that was treated with a hexamethyldisilazane (HMDS), and pre-baked at 100 °C for 90 sec to give a film thickness of 50 nm. The resulting wafer was developed with an 2.38 % aqueous trimethylammonium hydroxide (TMAH) solution at 23 °C for 30 sec. A static contact angle of resulting film against water was measured using a KYOWA Interface Science DropMaster 700.

3. Results and discussion

3.1. Resolution limit in CAR for hp 20 nm resolution and below

The E-beam exposure images for PBP at hp varied from 25 nm to 17.5 nm were summarized in Figure 1. Pattern collapse limited resolution below hp 20 nm. Such a collapse is usually observed in patterning of ultra-narrow lines, because capillary force associated with rinse water during drying step drastically increases with decreasing spacing of patterns. It is noteworthy that an image contrast degradation as a function of normalized-image log slope (NILS) and chemical blur originated from acid diffusion should not be key contributors for determining resolution because both a NILS of exposure tool and an acid diffusion of resist are controlled.

Figure 1. X-section images of PBP resist printed by E-beam (50 keV). HP of line and space is varied from 25 nm line/space to 17.5 nm line/space.

3.2. Resist design for high contact angle

The polymers synthesized in this study have a different hydrophobicity of protection groups and protection ratio as described in Table 1. Contact angles of resist film including each polymer were determined against water to estimate contact angle

at pattern sidewall during drying step. Figure 2 illustrates the relative contact angle of resist film against normalized protection ratio using these polymers. It clearly shows that contact angle is widely controllable by using polymers with different protection group and could be increased to $+20^\circ$ by utilizing polymer having the most hydrophobic protection group even at usable protection ratio for satisfying other requirements to polymer such as dissolution rate.

Figure 2. Relation between relative contact angle of resist film and normalized protection ratio. Usable protection ratio described by dashed line in the figure means the protection ratio which satisfy dissolution rate requirement to polymer.

3.3. Relation between contact angle and resolution: E-beam

Figure 3. Relation between ultimate resolution and contact angle of resist film. Vertical axis means resolution limit in which pattern collapse does not occur under E-beam exposure. *1 Contact angle θ was corrected by its pattern profile.

To elucidate origins of collapse, we exposed resists containing polymers with different contact angles by E-beam. Figure 3 plots the ultimate resolution in which pattern collapse does not occur against contact angle. In this figure, the contact

angle was corrected by its pattern profile (detailed procedures: see ref. 13). A linear relationship was observed between resolution and contact angle. This clearly indicates that hydrophobicity of resist, in other words capillary force, determines ultimate resolution of resist under E-beam exposure at hp 20 nm and below. Tight control of contact angle should be required to improve resolution also in the case of EUV exposure.

3.4. Demonstration of EUVL performances

Key attention is to demonstrate resolution of hp 20 nm and below using EUV exposure with satisfying LWR and sensitivity targets. Based on the results shown in section 3.2, we can design the new resist system where hydrophobicity of resist is sufficiently increased to satisfy requirement for reducing capillary force to prevent pattern collapse. Resolution capability of EUV resists with (i) resist A: highest contact angle ($+20^\circ$), (ii) resist B: higher contact angle ($+13^\circ$), and (iii) resist C: conventional contact angle ($+6^\circ$), were evaluated at 20 nm and below hp patterning using a Berkeley MET exposure system with a 45° rotated-dipole illumination ($\sigma_{\text{radius}} / \sigma_{\text{offset}} = 0.10 / 0.57, 0.3$) and 18 nm-dipole illumination, and summarized in Figure 4. As shown in Figure 4, resolution was improved from 24 nm to 20 nm by improving pattern collapse using resist B with higher contact angle ($+13^\circ$) compared with resist C with conventional contact angle ($+6^\circ$).

Figure 4. EUV patterning images at hp 20 nm and 18 nm for (i) resist B and (ii) resist C with 45° rotated-dipole illumination ($\sigma_{\text{radius}} / \sigma_{\text{offset}} = 0.10 / 0.57$) and 0.30 NA using a MET at SEMATECH Berkeley. Relative contact angles of resist B and resist C are $+13^\circ$ and $+6^\circ$, respectively.

Furthermore, 16 nm resolution and partial resolution down to 15 nm with line breaking were achieved for resist A with highest contact angle ($+20^\circ$) under pseudo-PSM dipole illumination (Figure 5). It is crucial that both LWR of 3.0 nm and sensitivity of 24 mJ/cm^2 at 18 nm hp pattern are reasonable for 20 nm and below hp device manufacturing with NXE: 3300 exposure tool for production. In consequence with these results, Z-

factor (Equation 1), which represents resist performance quantitatively according to equation 1,4 was $4 \times 10^{-9} \text{ mJ} \cdot \text{nm}^3$ for resist A with highest contact angle, and became to the best of our knowledge.

$$\text{Z-factor} = (\text{Resolution})^3 \times (\text{LER})^2 \times (\text{Sensitivity})$$

---(Equation 1)

Figure 5. EUV patterning images at hp 18 nm, 16 nm, 15 nm, and 14 nm for resist A (film thickness: 40 nm) with pseudo-PSM dipole illumination and 0.30 NA using a MET at SEMATECH Berkeley. Relative contact angle of resist A is $+20^\circ$.

Figure 6. Process window data at hp 20 nm for resist B (film thickness: 40 nm) with dipole 60X illumination (NA 0.25, $\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.83 / 0.41$). The inset summarizes lithography performances of resist B.

Full-field EUV exposure for resist B at hp of 20 nm using a NXE:3100 (NA 0.25, dipole 60X illumination ($\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.83 / 0.41$)) were collected to verify process window and summarized in Figure 6. This result demonstrates usable DOF of 200 nm at 10% EL at hp 20 nm patterning. Full-field EUV exposure imaging for resist A is now under evaluation.

3.5. Breakthrough technology for improving tradeoff between resolution and defectivity

Defectivity has received a great deal of attention in photolithography. It is well known that hydrophobicity of resist film affects density of blob type defect[14,15]. Figure 7 shows an

example of blob defect. There is no systematic study to investigate defectivity of blob as a function of contact angle of resist film.

Figure 7. An example of blob defect measured with defect inspection tool of KLA2360.

Figure 8. Contact angle dependency of density of blob type defect. After the open-frame exposure of resist film using a KrF light and development with this open-frame area, defect was counted with KLA2360 defect inspection tool.

Figure 8 illustrates density of blob defect versus contact angle of resist film. A clear threshold was observed for reducing blob defect below target of 0.1 counts/cm². Hydrophilic resist is strongly required for improving defectivity. This result is consistent with many previous reports. In contrast, hydrophilic resist results in poor resolution because of pattern collapse as discussed previously in section 3.3 and 3.4. A tradeoff relationship was clearly observed between resolution and defectivity.

Breakthrough technology to improve defectivity and resolution simultaneously is reforming properties of film surface from hydrophobic to hydrophilic during a lithography process before DIW rinse process because properties on pattern surface should be only associated with defectivity, not pattern collapse. Properties on pattern sidewall should be associated with pattern collapse because capillary force works

mainly at pattern sidewall. According to this hypothesis, we have developed a new EUV additive that reform only properties of film surface from hydrophobic to hydrophilic (Scheme 1), and defectivity data of the resist with this new EUV additive is summarized in Figure 9. This clearly shows that adding the new EUV additive to the hydrophobic resist reduced density of blob defect from 100 counts/cm² to below target of 0.1 counts/cm².

Scheme 1. Properties of film surface with a new EUV additive: hydrophobic after coating, and hydrophilic after exposure, PEB, and development processes.

Figure 9. Density of blob type defect for resist (a) without a EUV additive and (b) with a EUV additive. The data was taken from wafer that was exposed with a KrF laser and inspected with KLA2360 defect inspection tool.

4. Conclusions

Contact angle has been greatly increased by incorporating hydrophobic group in protection unit of polymer, and reached +20° by utilizing the hydrophobic group. Lithographic data with E-beam exposure clearly shows that resolution is improved by increasing contact angle of resist film. EUV exposure using MET at Berkeley demonstrates that the polymer with hydrophobic group can resolve hp 16 nm line/space with a reasonable sensitivity of 24 mJ/cm² and LWR of 3.0 nm. In accordance with these results, Z-factor reaches 4×10^{-9} mJ·nm³, which is the best of our knowledge and comparable with ITRS target of 1.0×10^{-9} mJ·nm³ for hp 18 nm. In addition, full-field exposure of the new polymer using NXE: 3100 at IMEC demonstrates usable DOF of 200 nm at 10% EL on hp 20 nm patterning. Newly developed EUV additive in which its polarity is changed from hydrophobic to hydrophilic only onto film surface successfully reduces a density of blob defect from 100 counts/cm² down to 0.1

counts/cm². These results indicate that our materials design provides a novel method to improve resolution without any degradation on LWR, sensitivity, and defectivity for hp 16 nm and below device manufacturing.

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