Negative-tone Imaging with EUV Exposure toward 13 nm hp

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Negative-tone imaging (NTI) with EUV exposure has major advantages with respect to line-width roughness (LWR) and resolution due in part to polymer swelling and favorable dissolution mechanics. In NTI process, both resist and organic solvents play important roles in determining lithography performances. The present study describes novel chemically amplified resist materials based on NTI technology with EUV using specific organic solvents. Lithographic performances of NTI process were described in this paper under exposures using ASML NXE:3300 EUV scanner at imec. It is emphasized that 14 nm hp was nicely resolved under exposure dose of 37 mJ/cm² without any bridge and collapse, which are attributed to the low swelling character of NTI process. Although 13 nm hp resolution was potentially obtained, a pattern collapse still restricts its resolution in case coating resist film thickness is 40 nm. Dark mask limitation due mainly to mask defectivity issue makes NTI with EUV favorable approach for printing block mask to produce logic circuit. A good resolution of CD-X 21 nm/CD-Y 32 nm was obtained for block mask pattern using NTI with usable process window and dose of 49 mJ/cm². Minimum resolution now reaches CD-X 17 nm/CD-Y 23 nm for the block. A 21 nm block mask resolution was not affected by exposure dose and explored toward low dose down to 18 mJ/cm² by reducing quencher loading. In addition, there was a negligible amount of increase in LCDU for isolated dot pattern when decreasing exposure dose from 66 mJ/cm² to 24 mJ/cm². On the other hand, there appeared tradeoff relationship between LCDU and dose for dense dot pattern, indicating photon-shot noise restriction, but strong dependency on patterning features. Design to improve acid generation efficiency was described based on acid generation mechanism in traditional chemically amplified materials which contains photo-acid generator (PAG) and polymer. Conventional EUV absorber which comprises of organic compounds is expected to have 1.6 times higher EUV absorption than polyhydroxystyrene based on calculation. However, observed value of acid amount was comparable or significantly worse than polyhydroxystyrene.

Keywords: EUV lithography, negative-tone imaging (NTI), chemically amplified resist, dark mask application, block mask, EUV sensitizer

1. Introduction

EUV lithography is one of the most promising candidates for half-pitch (hp) 16 nm device manufacturing and beyond [1]. The main challenges for EUV resist is to simultaneously satisfy resolution, line-width roughness (LWR), and sensitivity requirements according to ITRS roadmap [1-4]. While resolution of 13 nm line-space (L/S) pattern has been recently demonstrated using a chemically amplified resist (CAR) with an aqueous 2.38% TMAH developer, major limitation still exists on sensitivity [5-7]. Current sensitivity achievement reported so far is 37 mJ/cm² which is still higher than industry requirement of 20 mJ/cm² [8,9].

Sensitivity to keep imaging quality both on resolution and LWR is exacerbated as feature size decreases because of the photon-shot noise (PSN).
Our previous study revealed that sensitivity more than 30 mJ/cm² is necessary to obtain realistic pattern quality on 15 nm hp and below if we utilize conventional CAR resist and process [10]. Recently Kocsis et al., reported that some metal containing resists can print 9.5 nm L/S using EUV interference lithography tool, but this resist also needs ~50 mJ/cm² sensitivity [11]. As a brief conclusion, current EUV resists and processes have serious limitations on high volume manufacturing because industry requires both high resolution below 15 nm hp and high sensitivity below 20 mJ/cm². Key approach to improve this tradeoff relationship is increasing photo-activated materials during exposure to mitigate stochastic effects by PSN, hence many researchers have investigated metal containing resist to increase EUV absorption coefficient [12-15]. Although another method to overcome PSN is applying smoothing process [10], this approach is typically not acceptable with respect to resolution.

Major failure modes to print 13 nm hp are collapse, pinching, and bridging [16]. All of which are restricted by PSN, so features with L/S and contact hole patterns may be difficult to print with 20 mJ/cm² and below. On the other hand, effects of PSN is not clear on block mask pattern, which is proposed as an option to produce metal layer of logic device. This may be due to the primary interests so far with respect to EUV have been centered on the dark field mask and positive tone resists, i.e., L/S and contact hole application. Detailed understanding of low-dose NTI process with EUV exposure for block mask application helps to clarify beneficial approach to satisfy industry requirements.

NTI serves as a key enabling technology for imaging C/H and trench patterns in ArF immersion exposure because of advantage of optical contrast compared to positive tone imaging (PTI) [17-20]. Conversely, such NTI system advantages might be not useful for EUV exposure because wavelength of EUV light (13.5 nm) is enough short to optically resolve narrow trench and contacts. Only dark mask limitation due to mask density requirement from native mask defect makes NTI attractive for bright field application such as block mask. However, lack of systematic understanding has limited the utilization of NTI for EUV.

Selection of proper organic solvents in view point of solubility parameter opened up a route to address resolution below 15 nm hp L/S. Additionally, our recent study indicates possible that EUV-NTI is well applicable for narrow 20 nm dot printing [16]. However, there are still problems on sensitivity (L/S: 37 mJ/cm², dot: 46 mJ/cm²). Additional resist and process design are strongly required to meet industry requirements for both resolution and sensitivity (13 nm hp with 20 mJ/cm² sensitivity).

The present study aims to clarify how we can establish EUV lithography process by using NTI. Accordingly, we investigated lithography performance of NTI process on block mask and L/S with changing acid diffusion length and quencher loading of resist. The results are employed to design novel efficient resist materials for EUV lithography to breakthrough resolution and sensitivity tradeoff. Design to improve acid generation efficiency was also described based on acid generation mechanism in traditional chemically amplified materials which contain specific organic compounds as sensitizer.

2. Experimental
2.1. Materials

Conventional polarity switch platform to obtain hydrophilic film on exposed region has been used as a photoresist material. A series of protected co-polymer were synthesized according to the conventional polymerization methods [21]. A series of PAG with different cation structures were synthesized according to well known methods. An organic solution containing co-polymer, photo-acid generator (PAG), organic amine as a quencher, was prepared, and the resulting solution was filtered with a 0.03 um polyethylene filter prior to lithography performance evaluation. Developer and rinse materials were prepared using pure solvents without further purification unless otherwise noted.

2.2. Lithographic performance evaluation

The photoresist solution was filtered and spin-coated on a silicon wafer that was treated with an organic underlayer (UL) or spin on glass (SOG) stacked with spin on carbon (SOC), and the resulting film was pre-baked at 130 °C for 60 sec to give a specific film thickness for each patterning features. The wafer was exposed with either EUV light (13.5 nm) from an ASML NXE:3300 with 0.33 NA. After exposure, the wafer was baked (PEB) at moderate temperature for 60 sec, and developed with specific organic solvents at 23 °C for moderate time. The resulting wafer was rinsed.
with specific organic solvent to obtain negative-tone pattern. CD-SEM measurements were performed with a Hitachi CG5000 at imec.

Illumination condition of dipole 45X ($\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.902 / 0.671$) using the ASML NXE:3300 with 0.33 NA was used for giving a 1:1 L/S pattern. Similarly, dedicated illumination with $\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.848 / 0.307$ were used for block mask patterning on an ASML NXE:3300 with 0.33 NA.

2.3. Acid yield measurements by EB exposure

To determine acid generation yield, solutions containing polymer and PAG were prepared and filtered with an UPE filter. The resulting solution was spin-coated on silicon wafer, and prebaked at 130 °C for 60 sec to give a film thickness of 60 nm. The film was exposed by EUV with openframe at appropriated dose range, and extracted by an organic solvent. To a designated amount of solution including an acid-sensitive dye was added into the concentrated solution of extracted film. UV/Vis spectral changes were measured using a Shimadzu UV-2500 spectrophotometer to quantify generated acid amount as proton attached dye absorption.

3. Results and discussion

3.1. Lithographic performance achievement of NTI

Figure 1 shows exposure results of block mask to print CD-X of 21 nm dot by using Fujifilm CAR NTI resist (coating film thickness is 40 nm) with NXE:3300 scanner at imec. For this experiment, a specific rinse process was applied to bring resolution benefits on such a quite narrow pattern. CD-X value was obtained by averaging CD-X of three dots shown in the red rectangle. A good pattern profile was confirmed from CD-SEM image as shown in left figure. A wide DOF of 90 nm with 10 % EL was obtained with sensitivity of 49.1 mJ/cm², and minimum dot size reached CD-X of 18 nm. Although sensitivity was relatively high, this indicates a demonstrative advantage of NTI on block mask patterning. A part of the reasons is low swelling character of NTI solvents because a large tensile stress induced by swelling typically causes buckling-type deformation, and then causes peeling and breaking of patterns [22]. It is noteworthy that NTI process can directly print such a block mask pattern with dark field mask to avoid defectivity, whereas, PTI process needs bright field mask or inversion process for block mask.

![Figure 1. Block mask patterning data of NTI using a NXE:3300 with a dedicated illumination of $\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.848 / 0.307$. NTI process with FEVS-N series resist (40 nm coating thickness). Top image: best dose/focus image to get CD-X of 21 nm. Bottom figure: dose-focus window to print CD-X 21 nm block.](image1)

![Figure 2. Line/space patterning data of NTI using a NXE:3300 with a dipole 45X of $\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.902 / 0.671$. NTI process with FEVS-N series resist (40 nm coating thickness). Left image: 14 nm hp. Right image: 13 nm hp.](image2)
For fair comparison between NTI and PTI, L/S pattern has been printed using a NXE:3300 at imec with a dipole 45X illumination of $\sigma_{outer}/\sigma_{inner} = 0.902/0.671$. Figure 2 illustrates top-down CD-SEM images of 14 nm hp (left image) and 13 nm hp (right image) using NTI process. This is the first imaging data to obtain 14 nm hp L/S pattern using a conventional CAR platform for NTI process under EUV exposure with 37.0 mJ/cm$^2$ dosage. On the other hand, NTI could not print 13 nm hp L/S mainly due to pattern collapse and bridging. In comparison with reported imaging data of PTI, NTI is still behind it [9]. However, careful optimization of NTI process and resist formulation may bring 13 nm hp and below based on the resist study in later section.

### 3.2. Possibility to utilize fast sensitivity resist on block mask

A key attention is to realize if sensitivity benefits of NTI process exists or not on block mask application. To clarify sensitivity dependency, we formulated additional two resists by decreasing quencher loading to obtain ca 50% and 30% faster sensitivity than original resist. Table 1 summarizes block mask printing data of three resists with different sensitivity. All resists resolved 21 nm block pattern with similar pattern profile and usable process window (DOF > 80 nm at 10% EL). It is noteworthy that imaging quality seems to be kept when using faster sensitivity resist by 18 mJ/cm$^2$. This result is not consistent with our previous observation on 1:1 L/S pattern using PTI process in which fast sensitivity resist of 20 mJ/cm$^2$ resulted in worse resolution due mainly to pinching degradation. Similar tendency was observed for dense C/H printing using PTI resist as a degradation of local CD uniformity (LCDU) with decreasing exposure dose.

![Figure 3](image)

**Figure 3.** Relationship between sensitivity and minimum CD-X on dot (closed circle) and bar (open circle) at 21 nm block mask application. Exposed by NXE:3300 (NA 0.33) at imec with NTI process of FEVS-N series resist (40 nm coating thickness).

Correlation between sensitivity and minimum CD-X resolution on 21 nm block mask is illustrated in Figure 3. The minimum CD-X is kept almost same value even though sensitivity becomes faster than 20 mJ/cm$^2$, which is industry requirement from throughput. Similar tendency was also observed for minimum CD on bar

<table>
<thead>
<tr>
<th>Resist</th>
<th>Standard</th>
<th>Fast PR-1</th>
<th>Fast PR-2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sensitivity (mJ/cm$^2$)</td>
<td>48.2</td>
<td>27.1</td>
<td>18.3</td>
</tr>
<tr>
<td>DOF at 10% EL (nm)</td>
<td>100</td>
<td>105</td>
<td>80</td>
</tr>
<tr>
<td>DOF at dose to size (nm)</td>
<td>100</td>
<td>105</td>
<td>80</td>
</tr>
<tr>
<td>Minimum CD-X on dot to be resolved (nm)</td>
<td>18</td>
<td>18.7</td>
<td>19.1</td>
</tr>
<tr>
<td>Minimum line CD on long bar to be resolved (nm)</td>
<td>17.9</td>
<td>18.1</td>
<td>18.7</td>
</tr>
</tbody>
</table>

![Top-down CD-SEM Image on CD-X = 21nm dot](image)
structure. Major difference between the block mask data and past L/S data is pattern pitch and CD target. To clarify impact of pitch on LCDU-sensitivity tradeoff, several dot patterns were exposed by changing pitch from 60 nm to 175 nm with keeping target CD of 21 nm (mask CD is 28 nm). A tradeoff relationship was only observed for dense 60 nm pitch as shown in Figure 4a, and this is reasonable because low dose causes photon-shot noise and hence degrades imaging quality. On the other hand, no tradeoff relationship was observed for isolated 175 nm pitch.

It is surprising when considered with photo-shot noise because the shot noise should equally degrade imaging quality regardless of pitch. A possible explanation is that the pattern deformation during development exacerbates LCDU and resolution because expansion of dot pattern to cause CD variation, was mainly observed in dense dot pattern. This expansion is probably originated by interaction between the adjacent patterns as indicated by CD-SEM images (Figure 4b). This also indicates that current CAR NTI material still has a room to breakthrough the tradeoff relationship by optimizing dissolution properties. Another important notice is that isolated dot and block may be a suitable pattern layout to minimize impact of the shot noise in contrast with dense L/S, trench and contact hole. Continuous study including pattern transferability is proceeded using fast dose resist if block mask becomes a solution to produce semiconductor device with reasonable throughput and quality.

3.3. Influence of acid diffusion length
It is generally believed that acid diffusion control is a key method to overcome resolution, LWR and sensitivity tradeoffs in EUV lithography [23]. We have previously reported that combination of a high Tg and low Ea polymer with a large acid provides an apparently better L/S resolution with maintaining sensitivity [10,24]. In this study, we explored the same idea to determine how acid diffusion length contributes to block mask and isolated dot resolution.

Figure 4. a) Correlation between sensitivity and LCDU on dense dot (closed circle, pitch 60 nm) and isolated dot (open circle, pitch 175 nm) at 21 nm target CD (mask CD 28 nm). b) Comparison of CD-SEM images to print 21 nm dot and 19 nm dot by using slow resist and fast resist, respectively.

Figure 5. Plots of minimum dot CD versus EL at different pitch.

Exposure latitude for 1:1 L/S was used as indicator of acid diffusion length and plotted against minimum dot CD (Figure 5). As shown in Figure 5, higher EL was good for resolution.
regardless of pitch, indicating effectiveness of acid diffusion suppression to improve dot resolution. A similar improvement was observed on block mask as process window and minimum CD improvements as illustrated in Figure 6.

Figure 6. Process window of CD-X 21 nm block mask pattern by using (a) long acid diffusion resist and (b) short acid diffusion resist.

3.4. Resist approach to mitigate photon-shot noise effect: high acid yield design

Maximization of acid generation yield is important in EUV lithography to minimize impact of PSN on patterning quality. Sensitization mechanism of EUV resist has been well investigated by many researchers [25,26]. Absorption of high-energy EUV light (13.5 nm) mainly by polymer is the first step of EUV sensitization. Subsequent ionization of polymer and release of electron is next important step of the sensitization. This electron is then trapped by PAG through reductive electron transfer and activates PAG to generate acid. It has been reported that acid generation yield under EUV exposure is strongly affected by polymer structure [27-31]. PAG structure [32-34] and its loadings [33,34], respectively.

EUV absorption increase is becoming major interests to improve acid generation efficiency mainly due to the technical difficulty to enhance absorption coefficients of resist materials. It is well known that the absorption coefficient of EUV light is dependent on elements [12]. Therefore, much attention has been paid to metal containing resist to improve EUV absorption because conventional elements for traditional photoresists have relatively low absorption at EUV wavelength. On the other hands, some of elements in organic compound (e.g., antimony, fluorine, oxygen, bromine) have higher absorption than carbon atom. Therefore, we still have a room to enhance absorption coefficients by using modification of atoms in organic compounds. In this study, we have clarified potential availability of conventional organic elements based photoresist to improve acid generation yield against EUV light.

Figure 7. (a) UV/vis absorption spectral changes of resist following the EUV exposure and extraction using an organic solvent containing an acid-sensitive dye (b).

To quantify acid generation yield, we directly measured light-generated acid by the methods
described in experimental section. Figure 7(a) shows typical example of UV/vis absorption spectral changes of resist following the EUV exposure and extraction using an organic solvent containing an acid-sensitive dye. One new band around 480 nm attributable to proton adduct of the dye appeared with isosbestic points as the band of the dye decrease [18]. Absorption of the proton adduct of the dye was converted into the acid concentration using the standard curve between them, and an example of dose dependency of acid generation is shown in Figure 7(b). A linear relation was observed. This indicates that acid linearly increases as increasing exposure dose, and the slope of the plots corresponds to acid generation yield under exposure.

3.5. An example of dose dependency of acid generation

Six new model polymers were synthesized to investigate effect of EUV absorption on actual acid generation yield thru EUV exposure, and the experimental results are summarized in Table 2.

Table 2. Calculated EUV absorption and measured acid generation yield against EUV light for 6 new model polymers and polyhydroxystyrene (PHS) as a reference.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Relative EUV absorption coefficient (a.u.)</th>
<th>Relative EUV acid generation yield (a.u.)</th>
<th>Inefficiency calculated as &quot;1-(Acid yield/EUV abs.)&quot; (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHS</td>
<td>1.00</td>
<td>1.00</td>
<td>--</td>
</tr>
<tr>
<td>A</td>
<td>1.60</td>
<td>1.02</td>
<td>36%</td>
</tr>
<tr>
<td>B</td>
<td>1.32</td>
<td>0.90</td>
<td>32%</td>
</tr>
<tr>
<td>C</td>
<td>1.09</td>
<td>0.48</td>
<td>56%</td>
</tr>
<tr>
<td>D</td>
<td>1.02</td>
<td>0.80</td>
<td>22%</td>
</tr>
<tr>
<td>E</td>
<td>1.33</td>
<td>0.71</td>
<td>47%</td>
</tr>
<tr>
<td>F</td>
<td>1.20</td>
<td>1.10</td>
<td>8%</td>
</tr>
</tbody>
</table>

A relatively large gap was observed between calculated EUV absorption coefficient and actual acid generation yield depending on the polymer. Energy of incident EUV light is consumed upon secondary electron generation according to the energy level of emissive electron, therefore, normally there is a ~ 10 % loss of electron against excitation of carbon atom. In addition, effects of the absorption coefficient difference are theoretically reduced as a result of electron absorption through optical path (depending on film thickness). However, the observed data indicates that there are the other inefficient processes which waste the generated electrons because the inefficiency in Table 2 is significantly large and dependent on polymers.

There are two possible explanations: i) fast decomposition of polymer on electron attachment, ii) lower LUMO energy of polymer than that of PAG. Based on DFT calculation, it was confirmed that case i) is actually possible inefficient path to waste generated electrons. Figure 8 shows relationship between acid generation yield and LUMO energy of the polymers which contains similar backbone. LUMO energy is plotted as a relative value from that of PAG. The inefficiency became higher as shifting LUMO energy of polymer more to negative value. This is reasonable because lower LUMO than PAG would cause electron cascade from PAG to polymer, and this stabilize electron and prevent PAG decomposition through the electron attachment. This result provides us important conclusion that suitable materials design has a possibility to further improve acid generation yield as expected from EUV absorption.

Figure 8. Plots of EUV acid generation yield and LUMO energy of polymers B, D, E which contain similar backbone. LUMO energy is plotted as a relative value from that of PAG.

4. Conclusions

The present study clearly demonstrates potential advantage of NTI process to utilize it for bright field application such as block mask where positive-tone imaging process is not favorable with respect to mask defectivity. A 21 nm block mask resolution was confirmed and explored toward low exposure dose below 20 mJ/cm² using a traditional
CAR for NTI. A part of the reasons may be attributed to the less swelling character of exposed resist film as well as the lower surface tension of the solvent used (compared to PTI). Accordingly, NTI process for EUV provides a novel route to print narrow pitch with a reasonable sensitivity of 20 mJ/cm² and a practical process window for continuous shrinkage of semiconductor devices. On the other hand, limitations to L/S resolution is attributable to microbridging as the root cause, and the NTI process still needs optimization toward 13 nm hp L/S resolution.

The present study has also shown the ability to improve sensitivity by carefully control properties of PAG and polymer. An EUV absorption enhancement by increasing absorption coefficient against EUV light seems to be useful way for improving acid generation yield, however, careful manipulation of electronic properties is necessary to effectively activate PAG at current CAR EUV resist. This indicates that application of metal containing materials, therefore, does not simply result in improvement on stochastic effect induced by PSN.

Acknowledgements

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References


