Manipulation of dissolution properties by changing organic solvent developer and rinse material provides a novel technology to obtain fine pattern beyond the limitation of imaging system based on alkaline developer. QCM study showed no swelling character in negative-tone imaging (NTI) process even for current developer of n-butyl acetate (nBA). Actually, NTI process has shown advantages on resolution and line-width roughness (LWR) in loose pitch around 30 ~ 45 nm hp as a consequence of its non-swelling character. On the other hand, bridge and collapse limited its resolution below 20 nm hp, indicating that non-negligible amount of swelling still exists for tight pitch resolution. We investigated effects of solubility parameter of organic solvents on resolution below 20 nm hp. A bridge was reduced with a decrease in the solubility parameter \( \delta_p \) from nBA. On the other hand, much lower \( \delta_p \) caused film remaining due to its extremely slow Rmax. Based on these results, we newly developed FN-DP301 containing organic solvent with smaller \( \delta_p \) than nBA. Although rinse solvent gave negligible effects on bridge, there is a clear improvement on pattern collapse only in case of using new rinse solvent of FN-RP311.

Lithographic performances of NTI process using nBA and FN-DP301 together with the other organic solvents were described in this paper under exposures with an E-beam and a EUV light. It is emphasized that 14 nm hp resolution was obtained only using FN-DP301 as a developer and FN-RP311 as a rinse under E-beam exposure. NTI showed 43\% faster photospeed in comparison with PTI at 16 nm hp, indicating that NTI is applicable to obtain high throughput with maintaining resolution. In addition, sub-20 nm trench was obtained using NTI without bridge under EUV exposure, all of which are attributed to the low swelling character of NTI process. Similarly, NTI was able to print 20 nm dots using NXE:3100 with only a little peeling. Conversely CH patterning was significantly worse with NTI compared to PTI, that is, only 36 nm contacts with 60 nm pitch was resolved under EUV exposure.

Keywords: EUV lithography, negative-tone imaging (NTI), chemically amplified resist

1. Introduction

EUV lithography is one of the most promising candidates for half-pitch (hp) 20 nm device manufacturing and beyond.1 The main challenges in the development of an EUV resist that will satisfy the ITRS roadmap is the combination of matching resolution, line-width roughness (LWR), and sensitivity, simultaneously [1-4]. While resolution of a line-space (L/S) pattern at 14 nm hp has been recently demonstrated using a chemically amplified resist (CAR) with an aqueous 2.38\% TMAH developer using EUV exposure tool [5-7], limitations to sub-14nm resolution exist due primarily to pattern collapse. Pattern collapse is
exacerbated as feature size decreases because of the strong capillary force present with the use of aqueous based developers. Although one method to overcome pattern collapse is to reduce the film thickness of resist, the thinning of resist to 25 nm or below is typically not acceptable with respect to pattern transfer to the substrate.

It is well known that pattern collapse is impacted by capillary force, mechanical strength of the photoresist, and adhesion to the substrate [8]. Accordingly many researchers have investigated film thickness, surface tension solvents used as developers or rinses, adhesion property of substrates and underlayers, as well as hydrophobicity and mechanical strength of photoresists for their ability to decrease the capillary force [9-10]. To date, there have been only one report with respect to how pattern collapse can be mitigated with an organic solvent developer resulting in the NTI [11]. This may be due to the primary interests so far with respect to NTI have been centered on the optical advantage towards patterning both contact hole (CH) and trench patterns using a bright field mask. Additionally, recent report indicated that bridge between printed features restricts fine pattern formation despite having a high optical contrast in EUV lithography [12]. However, detailed understanding is still lacking how we can mitigate both collapse and bridge to satisfy industry requirements.

NTI serves as a key enabling technology for imaging trench and CH patterns in ArF immersion exposure because of advantage of optical contrast compared to positive-tone imaging (PTI) [13-16]. Such NTI process advantages might be useful for EUV exposure to print trench and CH as well and our previous simulation analysis supported this, indicating that NTI had a specific advantage of high photon density while keeping optical contrast for CH in an ideal case of low EUV flare condition [17]. However, verification of the sensitivity-resolution advantage using an actual EUV scanner with a moderate flare has not yet been performed. Furthermore, lack of systematic understanding of its dissolution properties during development has limited the utilization of NTI process only for bright mask application like ArF immersion even though target features of EUV becoming more and more stringent.

The present study aims to clarify how we can improve lithography performance of EUV lithography by using NTI process. Accordingly, we investigated dissolution properties of NTI in comparison with PTI to make clear the fundamental advantages of NTI, and the obtained results are employed to design novel efficient developer and rinse material for EUV lithography. Various kind of organic solvents with a different solubility parameter have been prepared as a developer and rinse material to identify best performer for EUV lithography. Lithographic performance comparisons of L/S, iso trench, iso line, and CH have been reported using an EUV scanner and a point-beam EB tool.

2. Experimental

2.1 Materials

Conventional polarity switch platform to obtain hydrophilic film on exposed area has been used as a photoresist material. A series of protected co-polymers were synthesized according to the conventional polymerization methods [18]. 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 μm 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) and 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:3100 with 0.25 NA and a small-field exposure tool (SFET) at EIDEC with 0.30 NA, or a point-beam EB tool of JEOL JBX6000FS/E (Vacc = 50 keV) at Fujifilm and Elionix ELS-F125 (Vacc = 125 keV) at NIMS (National Institute for Materials Science). After exposure, the wafer was baked (PEB) at moderate temperature for 60 sec, and developed with seven different organic solvents including nBA as a reference at 23 °C for moderate time. The resulting wafer was rinsed with two different rinse materials to obtain negative-tone pattern. As a reference, a 2.38 % TMAH aqueous solution and surfactant containing rinse material as a developer and rinse material, respectively was used to obtain positive-tone pattern. CD-SEM measurements were performed with a Hitachi CG5000 for EUV exposure or a Hitachi S4800 for EB exposure.
Illumination condition of dipole 60X ($\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.81 / 0.43$) using the ASML NXE:3100 with 0.25 NA was used for giving a 1:1 L/S pattern. Similarly, conventional illumination with $\sigma = 0.51$ and quasar illumination with $\sigma_{\text{outer}} / \sigma_{\text{inner}} = 0.51 / 0.51$ were used for trench and CH patterning on an ASML NXE:3100 with 0.25 NA. The 1:1 L/S pattern with hp of 50 nm, 30 nm, 20 nm, 18 nm, 16 nm, 15 nm, and 14 nm was drawn using a JEOL JBX6000FS/E EB tool.

2.3 QCM analysis

Mass variation of resist film during development step was measured by a quartz crystal microbalance (QCM) method with a Litho Tech Japan QCM QZ-3 system at 23 °C (substrate is 5 MHz quartz resonators with a gold electrodes). In the QCM measurements, various kind of organic solvents and a 2.38 % TMAH were used as developer to monitor the mass variation of resist coated film (thickness: 100 nm). Average dissolution rates were calculated using a period of time for film clearing. To analyze swelling behavior, QCM data were collected on exposed resist film which was prepared under EB exposure at the specific dose prior to the QCM measurement.

2.4 Solubility parameter estimation

Solubility parameters (SP) of polymers were experimentally obtained from the precipitation method described below. A small amount of polymer was added into 10 ml of tetrahydrofuran (THF). To the resulting polymer solution, water was added dropwise to obtain cloud points $V_{mh}$ as a poor solvent with high SP. In a similar manner, hexane was added dropwise to obtain cloud points $V_{ml}$ as a poor solvent with low SP, separately. It has been reported that the solubility parameter can be estimated by the following equations [19]:

$$\delta = \frac{1}{2} \times \frac{[(\text{VTHF} \cdot \delta_m - \text{THF} + V_{mh} \cdot \delta_{mh}) / (\text{VTHF} + V_{mh})] + [(\text{VTHF} \cdot \delta_m - \text{THF} + V_{ml} \cdot \delta_{ml}) / (\text{VTHF} + V_{ml})]}$$

where $m = p$: polar force, $h$: hydrogen bonding force, $d$: dispersion force of solubility parameter, VTHF = volume of THF (ml), $V_{mh}$ = necessary volume of water to reach cloud point (ml), $V_{ml}$ = necessary volume of hexane to reach cloud point (ml), $\delta_m$ = solubility parameter of THF, $\delta_{mh}$ = solubility parameter of water, $\delta_{ml}$ = solubility parameter of hexane; see reference 19 about solubility parameter of solvents used in this study.

3. Results and discussion

3.1. Dissolution characteristics of NTI

Figure 1 a shows a typical example of in-situ QCM resonant frequency behavior which is observed during the development process. When nBA is used as the developer, no appreciable signals were observed in the negative region, indicating that dissolution proceeded immediately after penetration of the developer into film and that swelling did not occur at all exposure dose ranges. Figure 1b shows similar QCM monitoring data with an aqueous 2.38 % TMAH solution. Conversely, the aqueous QCM data clearly shows that swelling occurs and is evidenced by the observation of waves within the negative region throughout all exposure regions except for the highest dose region (where dissolution is at its maximum rate).

Figure 1. QCM wave changes in (a) a nBA solvent as NTI developer and (b) an aqueous 2.38 % TMAH as PTI developer. Exposure dose of EB is from 0 $\mu$C/cm² to 7 $\mu$C/cm² with step of 1 $\mu$C/cm². Inset means enlarged view with range of from 0 to 40 in development time (x axis) and from 0 to −100 in $\Delta$ frequency (y axis). Negative value in QCM corresponds to gel layer formation (i.e., swelling).
This swelling phenomena can be explained when considering the development process using 2.38% TMAH and nBA because: (i) the drive towards acid-base equilibrium formation between methacrylic acid and TMA+ enhances the rate of penetration by alkaline developer into the de-protected resist film, the subsequent solvation and migration of the polymer chain through the bulk developer layer is slower than the rate of penetration by alkaline developer resulting in increased swelling within the photoresist film. On the other hand, (ii) such acid-base equilibrium state is not observed with nBA developer due to the lower polar character of the organic solvent. The low polarity of nBA favors the dissolution of the protected photoresist and leaves the exposed region (de-protected photoresist) on the wafer. The rate of penetration by nBA into the protected photoresist film is comparable to the dissolution rate of the solvated polymer chain and results in no swelling within the film.

3.2. Efficient NTI developer design

In previous work, we revealed that nBA had a clear advantage on dissolution unit grains size and surface smoothness compared to aqueous 2.38% TMAH solution [20]. Similarly, we demonstrated LWR advantage of nBA when exposing conventional polarity switch photoresist with 45 nm hp L/S [20]. On the other hand, similar patterning results on both developers have been confirmed when feature size is 20 nm hp and photoresist is cross-linking systems.

Two important questions now arise, (1) are the NTI process using nBA developer indeed ideal process to resolve a tight pattern below 20 nm hp? If no, (2) what is an optimal developer to bring out performance benefits of an organic solvent system to the maximum?

Figure 2 shows typical examples of contrast curve which are collected by using organic solvents as developers and a model EUV resist under KrF exposure. All developers consist of pure organic solvents. We widely changed solubility parameter of organic solvents and investigate its effects on the dissolution property of EUV resist. Figure 3 summarizes dissolution contrast of several organic solvents for a model EUV resist. The organic solvents divide into three groups: 1) solvents which show dissolution contrast, 2) solvents which don’t show dissolution contrast due to film remaining on non-exposed area, 3) solvents which don’t show dissolution contrast due to entire film dissolution on exposed area. Solvents with higher polar force ($\delta_p$) than 1.2 results in complete dissolution of resist film regardless of exposure, indicating that polarity change of conventional polymer is relatively small when using the polar solvents. The similar explanation is also applicable for the dissolution behavior of less polar solvents which have smaller $\delta_p$ than 0.82, because this is too hydrophobic to make contrast for the current polarity switch polymer platform. Key finding is that solvents with a proper polarity force and dispersion force, which is indicated by dashed circle in Figure 3, is only workable as a developer for the current EUV polymer. A typical NTI developer of nBA for both ArF and EUV actually showed dissolution contrast. Another important point is that the FTL in Figure 2 is dependent upon both $\delta_p$ and $\delta_d$, moving to less FTL in the following order: solvent C > nBA (FN-DP001) > solvent B > solvent A (FN-DP301). This indicates that solvent A is one candidate to have a minimum FTL character over pure organic solvents.
Figure 3. Dissolution characters of a model EUV resist against various kinds of organic solvents with a different solubility parameters. δp and δd mean polar force and dispersion force of solubility parameter, respectively. Closed circle means organic solvent that shows contrast after development (exposed area: remain, non-exposed area: fully dissolve away). Closed rectangle means solvent that didn’t show contrast due to film remaining both for exposed and non-exposed area. Solvent that didn’t show any contrast due to entire film dissolution is represented by open circle.

Lithography performance of a model EUV resist was evaluated using six different kinds of organic solvents as NTI developer with EB exposure to obtain information about the optimal developer design for resolution beyond 14 nm hp, and results are summarized in Figure 4. Surprisingly, nBA didn’t resolve fine pattern below 20 nm hp due mainly to bridge and collapse. It clearly shows that ultimate resolution strongly depends on developer and become better when using a developer in the order: nBA < solvent B < solvent E < solvent A. This is consistent with the observed FTL shown in Figure 2, i.e., smaller FTL causes better resolution. It is noteworthy that solvent A, named as “FN-DP301”, showed a 43% higher sensitivity than nBA with better resolution down to 16 nm hp. This indicates that adequate design of developer is a key enabler to breakthrough well-known resolution-sensitivity tradeoff in EUVL [21]. A possible explanation to better resolution with FN-DP301 (solvent A) versus nBA is the low swelling character in the FN-DP301, since both bridge and collapse within narrow L/S pattern can manifest through excessive swelling of pattern. Difference of swelling nature between FN-DP301 and nBA is not evident, but clear correlation between resolution and FTL may suggest importance of Rmin to suppress swelling. In other words, slow Rmin should give a low developer affinity for exposed film and hence enhances both swelling and dissolution contrast to obtain good resolution.

<table>
<thead>
<tr>
<th>Developer</th>
<th>Product</th>
<th>Cross-section image at optimum dose</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>--</td>
<td>not resolved not resolved not resolved not resolved not resolved not resolved</td>
</tr>
<tr>
<td>nBA</td>
<td>FN-DP001</td>
<td>167</td>
</tr>
<tr>
<td>B</td>
<td>--</td>
<td>129</td>
</tr>
<tr>
<td>E</td>
<td>--</td>
<td>120</td>
</tr>
<tr>
<td>A</td>
<td>FN-DP301</td>
<td>96</td>
</tr>
<tr>
<td>D</td>
<td>--</td>
<td>not resolved not resolved not resolved not resolved not resolved not resolved</td>
</tr>
</tbody>
</table>

Figure 4. Dense 1:1 L/S printing results of NTI using six kinds of developers. EB drawing to give each hp of pattern.
It has been well-known that dissolution contrast of NTI process is lower than that of PTI process because NTI doesn’t include acid-base equilibrium between methacrylic acid and TMA⁺ which drastically promote dissolution of polymer into developer. There have been numerous efforts to enhance dissolution contrast of NTI process by optimizing materials both in polymer and developer [22-24]. Recent report indicated that dissolution contrast enhancement by an ionic-contrast enhancer is effective to improve resolution when we adequately select proper resist platform, but swelling behavior when using the ionic-contrast enhancer may limits future application of this method [24].

A key design should be to achieve high dissolution contrast with keeping a good swelling property. To establish a truly effective route for designing high dissolution contrast material, we collected dissolution rate data with varying polymer solubility parameter and developer solubility parameter, individually. Figure 5 summarizes dissolution rate against difference of solubility parameter between polymer and developer (ΔSP, shown in following equation). Solubility parameter of polymers was collected according to the method described in section 2.4.

A good correlation between ΔSP and dissolution rate was observed for each plots. This is reasonable because dissolution of polymer against organic solvent should depend on dissolution energy of materials when dissolution step includes only a simple solvation by dispersion, polar, and hydrogen bonding interactions. On the other hand, each plot has distinct slopes: closed circle = 0.45, open circle = 1.28. This shows that dissolution rate can be widely changed by changing solubility parameter of developer rather than polymer. As a result, 1/10 times slower dissolution rate was obtained by using FN-DP301 as a NTI developer. This is not expected, but maybe explained by considering influence of penetration step in which size of developer may play an important role. In conclusion, adequate design of developer should become more important to obtain proper and minimal swelling since minimum feature size is becoming more and more narrow.

3.3. Rinse material design for collapse mitigation

It is well known that pattern collapse is mainly affected by capillary force, and that the force can be quantitatively represented by Equation 1. As indicated by this equation, capillary force increases as the spacing between adjacent photoresist lines decreases. Therefore as feature size continues to shrink the capillary forces experienced by the photoresist will increase unless contributory factors are found which will offset or reduce the increasing force. One advantage of NTI process is the lower surface tension (γ) of the developer, ~25 dyn/cm for nBA, compared to ~72 dyn/cm for PTI.

$$F = \frac{2\gamma \cos \theta}{d} \frac{hl}{d}$$

(Eq. 1)

Figure 6 summarizes lithography performance of rinse materials to resolve 1:1 L/S under EUV exposure and physical properties of the rinse materials. In case of without rinse condition, nBA developer should act as rinse material because remaining solvent before drying is developer itself in this case. It is surprising that collapse behavior of FN-RP002 and RP311 was obviously different with each other, though calculated capillary force was similar with each other. New rinse material, FN-RP311, showed significant improvement on pattern collapse, and resolution was not limited by collapse in this case even for 21 nm hp which is optical contrast limit of this exposure system. On the other hand, our conventional rinse material of FN-RP002 didn’t improve pattern collapse at all as well as rinse-less process. Even for NTI process which involves low surface tension organic solvents, adequate rinse material is necessary to improve pattern collapse. Newly developed FN-RP311 is a promising candidate for improving pattern collapse in 1:1 L/S, due primary to its low swelling character.
Comparison of the ultimate resolution between NTI and PTI has been performed using EB to gain mechanistic insight into this phenomenon. HP of 16 nm was drawn for this purpose because resolution limit of this tool is around 18 nm. It should be noted that best rinse materials were used for both PTI and NTI platforms in this ultimate resolution testing. FN-RP311 was used for NTI, while a surfactant containing water with surface tension of 40 mN/m was applied as rinse material in the PTI. Figure 7 shows the cross section SEM image of NTI compared to that of PTI, both of which are optimized against each process. As seen in Figure 7, NTI was able to achieve the same resolution with our current best PTI system. Although resolution in both processes was equivalent to each other, it is noteworthy to point out that height of the remaining photoresist line was greater for NTI (28 nm) compared to the 22 nm height of the PTI photoresist pattern. Pattern height is an important aspect of resist performance as well as a contributor to the capillary force experienced by the photoresist lines. We can conclude that collapse performance of NTI is better than PTI, with respect to 1:1 L/S performance. A complete understanding of the reasons why NTI has better collapse behavior is still being investigated, but part of the reasons should be attributed to the less swelling character of NTI, only in case for FN-RP311. Moreover, sensitivity to obtain this image was 43% faster in NTI, i.e., 96 µC/cm² for NTI, while 170 µC/cm² for PTI. Sensitivity of 96 µC/cm² in EB corresponds to 20 mJ/cm² in EUV. These results indicate potential benefit of NTI to obtain high throughput with maintaining resolution by breakthrough RLS tradeoff.

<table>
<thead>
<tr>
<th>Developer</th>
<th>Rinse</th>
<th>Ultimate resolution (nm)</th>
<th>Surface tension, γ (mN/m)</th>
<th>Contact angle, θ (degree)</th>
<th>Capillary force, F</th>
<th>30 nm hp</th>
<th>25 nm hp</th>
<th>23 nm hp</th>
<th>21 nm hp</th>
</tr>
</thead>
<tbody>
<tr>
<td>nBA</td>
<td>None</td>
<td>25</td>
<td>25</td>
<td>&gt; 30 (not measurable)</td>
<td>&lt; 43</td>
<td>25</td>
<td>25</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>nBA</td>
<td>FN-RP002</td>
<td>25</td>
<td>25</td>
<td>&gt; 30 (not measurable)</td>
<td>&lt; 43</td>
<td>25</td>
<td>25</td>
<td>23</td>
<td>21</td>
</tr>
<tr>
<td>nBA</td>
<td>FN-RP311</td>
<td>22</td>
<td>20–25</td>
<td>&gt; 30 (not measurable)</td>
<td>&lt; 43</td>
<td>22</td>
<td>20–25</td>
<td>23</td>
<td>21</td>
</tr>
</tbody>
</table>

Figure 6. Comparison of EUV lithography performances of three rinse conditions using a SFET (NA 0.3) at EIDEC with an annular illumination (σ 0.7/0.3). Physical properties of rinse solvents are also summarized.

Figure 7. Cross section images of a) PTI (left) and b) NTI (right). EB drawing to give a 16 nm line/space with initial film thickness of 30 nm for PTI and 40 nm for NTI. Dose is 170 µC/cm² for PTI, while 96 µC/cm² for NTI.
In order to clarify potential advantages of NTI process, ultimate resolution data was collected by optimizing EB drawing method (for example, mask bias) and resist formulation. Figure 8 illustrates 14 nm hp imaging data of our latest EUV-NTI resist of FEVS-N1500C using a FB-DP301 and FN-RP311 as developer and rinse solvent, respectively. It is interesting to note that conventional CAR platform with an optimal NTI process is able to resolve 14 nm L/S pattern without pattern collapse with a 220 μC/cm² which corresponds to 50 mJ/cm² sensitivity in EUV. Remaining film thickness of 25 nm again demonstrates collapse advantage of new NTI process which has minimal swelling character. These results indicate the possibility of extending CAR as industry acceptable approach beyond 14 nm hp.

Figure 8. HP 14 nm imaging data of FEVS-N1500C using a FN-DP001 and FN-RP311 as developer and rinse solvent, respectively. Data was collected under EB drawing using an Elionix ELS-F125 (Vacc = 125 keV) at NIMS with initial film thickness of 40 nm on an under layer.

3.4. Patterning capability on L/S, trench and CH with a comparison against PTI

In order to elucidate the overall advantage of the NTI process in EUV, for example trench printability, and dot and CH patterning capability, full-field EUV exposure was performed using a NXE:3100 (NA 0.25) with (a) conventional illumination (σ= 0.51) for trench, and (b) quasar illumination with σouter / σinner = 0.81 / 0.51 for dot and CH. For these experiments, only nBA (FN-DP001) was applied as developer, and rinse material was not applied.

Trench performance was investigated using a mask of 30 nm line on pitch 120 nm with an under exposure. This demonstrates that NTI resist can resolve trench patterns around 18 nm without microbridging. PTI was unable to resolve such a narrow trench due to severe bridging. This tendency is similar to ArF immersion case [14, 25], but the origin should be different with ArF because optical image quality of NTI was similar with PTI in this case. Let us emphasize the following points that trench-width roughness (TWR) became better as decreasing trench size in case of NTI, though TWR of PTI became worse remarkably as shown in Figure 9b. A possible explanation to better bridging performance with NTI versus PTI is the low swelling character in the NTI process, since bridging within narrow trenches can manifest through excessive swelling of pattern.

Figure 9. Trench performance data of NTI (top): 30 nm line on 120 nm pitch (in mask) at film thickness 45 nm in comparison with PTI: 30 nm space on pitch 120 nm with an under exposure. This demonstrates that NTI resist can resolve trench patterns around 18 nm without microbridging. PTI was unable to resolve such a narrow trench due to severe bridging. This tendency is similar to ArF immersion case [14, 25], but the origin should be different with ArF because optical image quality of NTI was similar with PTI in this case. Let us emphasize the following points that trench-width roughness (TWR) became better as decreasing trench size in case of NTI, though TWR of PTI became worse remarkably as shown in Figure 9b. A possible explanation to better bridging performance with NTI versus PTI is the low swelling character in the NTI process, since bridging within narrow trenches can manifest through excessive swelling of pattern.
Process window for 26 nm dots using a dark mask comprises of 31 nm contacts and 52 nm pitch is shown in Figure 10. A wide DOF of 180 nm with 8 % EL was obtained, and minimum dot size reached to 21 nm. Although sensitivity was relatively high (i.e., above 50 mJ/cm²), there is a demonstrative advantage on minimum pillar size even in case of rinse-less process. As discussed in the previous section, collapse was significantly improved by applying new rinse of FN-RP311 due to its low swelling character. Similar improvement is expected also for peeling-type failure of pillar pattern because a large tensile stress induced by swelling typically causes buckling-type deformation, and then causes peeling [26]. We have no fair comparison data with PTI, but less swelling character of NTI indicates potentially useful application of NTI to pillar/dot patterning for not only single patterning application but also multiple patterning application with 1D layout and block mask.

Conversely, NTI didn’t print narrow contacts. Dense CH data were collected using a bright mask of 30 nm dots on pitch 60 nm with varying exposure dose, and the data are summarized in Figure 11.

Compared to the corresponding PTI data reported so far, NTI showed worse performance. NTI was unable to resolve contacts of pitch 60 nm, while PTI was able to resolve contact holes below pitch 52 nm [27]. This performance may be driven by large flare of such a bright mask and additional experimentation is underway to understand this phenomena.

Figure 11. Dense CH printing results of NTI under EUV exposure by NXE:3100 with a quasar illumination of σouter / σinner = 0.81 / 0.51.
4. Conclusions

This study has shown the fundamental advantage of NTI process with respect to swelling property for fine pattern formation. nBA is an effective NTI developer and has less swelling character compared to an aqueous 2.38% TMAH solution which is a typical PTI developer. However, nBA might not be an optimal developer as the minimum feature size decreases to below 20 nm hp. Newly developed FN-DP301, which has an optimal solubility parameter in $\delta_p$ and $\delta_d$ compared with nBA, acts as an efficient developer with respect to resolution, indicating that swelling can be further reduced by manipulating developer properties. Accordingly, good L/S performances down to 14 nm hp, with a greater film thickness retention, were observed only for NTI process using FN-DP301. It is noteworthy that FN-DP301 gave a 43% faster Esize in comparison with PTI.

The present study clearly demonstrates fundamental advantage of NTI process to utilize it not only for bright mask application that has optical contrast advantage, but also for dark mask application. Additionally, these results demonstrate that NTI process can be utilized as a novel method to achieve continuous shrinkage of semiconductor devices beyond limitations of PTI process. Additional resist and process design are necessary to address below 12 nm L/S patterning and CH patterning challenges.

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