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# PHOTOMASK

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PM16-Best Poster Paper

## Investigation of fabrication process for sub 20-nm dense pattern of non-chemically amplified electron beam resist based on acrylic polymers

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### ABSTRACT

In this study, we examine exposure characteristics of a positive tone electron beam resist consisting of methyl  $\alpha$ -chloroacrylate and  $\alpha$ -methylstyrene by changing the development process conditions. 25/25nm and 30/30nm line-and-space (L/S) patterns (design value) are developed in amyl and heptyl acetates. The resist patterns developed at 0°C for 120 s show the better shapes having the vertical sidewalls than those developed at 22°C for 60 s. The dose margins of pattern formation for 0°C development become wider, although the sensitivities are lower. The effect of post exposure baking (PEB) on exposure characteristics is also investigated. Adding PEB process performed at 120°C for 2 min, the dose margin also becomes wider although the sensitivity is lower. 20/20nm L/S patterns are fabricated by using PEB and/or 0°C development. Though the required exposure dose is larger, the resist pattern is improved by PEB and/or 0°C development. The formation of 35nm pitch pattern is also presented.

### 1. Introduction

In the case of the multi-beam mask writer with an acceleration voltage of 50 kV, a line-and-space (L/S) pattern resolution of 20nm is required for next generation photomask fabrication.

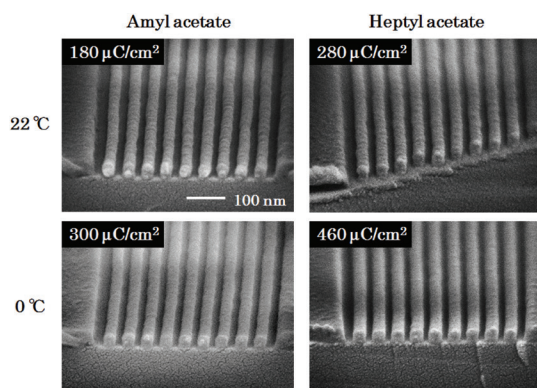


Figure 1. SEM images of 25/25nm L/S pattern developed in amyl at 22°C, amyl at 0°C, heptyl at 22°C and heptyl at 0°C.

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# EDITORIAL

## Maskmaking – 50 Years of History in Enabling Moore’s Law Will Continue with EUV

Janice Golda, Intel

If a picture is worth a thousand words, how many words is a photomask worth? SPIE’s 2017 Advanced Lithography Conference is underway and Dr. Frank Abboud, Vice President Technology Manufacturing Group and General Manager, Intel Mask Operation kicked off his keynote presentation “Photomask Technology Challenges for Upcoming technology Nodes” by comparing the amount of digitized data in a 14nm photomask to that in a two hour HD movie. A six inch square 14nm photomask contains more images than ten HD movies...that’s a lot of pictures! Loading this photomask onto a cutting-edge immersion scanner creates the world’s fastest form of data transfer, outrunning other methods of data transfer from 5G to optical links by four orders of magnitude. This ability to transfer massive amounts of data quickly to the wafer has been an important enabler of Moore’s Law for the past five decades and will continue to be so for the foreseeable future.

Abboud progressed to explain the evolution of photomask technology, from contact printing up through extreme ultraviolet lithography (EUVL). Contact printing and later proximity printing enjoyed mainstream use in the 1960’s and 1970’s. 1X projection masks took over proximity printing masks due to proximity’s inability to keep masks defect free. This theme of zero defect masks will prove to be a persistent one for years to come. Maskmaking blossomed in the 1980’s with over 200 writers capable of printing photomasks with feature sizes equal to those on the wafer. Many companies developed e-beam writers to support this market. The mid 1980’s saw the introduction of 5x reduction lithography steppers: this provided a ten year “holiday” in resolution, but the smaller number of die per mask meant that zero defect masks were “must have”.

The maskmaker’s holiday ended in the late 1990’s, when lithographers began printing features smaller than the wavelength of the 193nm light in the scanner. This motivated several new mask technologies. Phase shift masks (PSM) became common, and required writing and etching multiple layers on a photomask. Abboud shared the insight that laser based mask writers had existed since the mid 1980’s as fast, loose layer tools, but their ability to write patterns without charging up the mask proved to be a PSM technology enabler. On the e-beam side, stringent pattern fidelity and resolution enhancements drove the transition from 10keV to 50keV e-beam, and 50keV drove introduction of chemically amplified resists into the mask shop to enable faster write times with less heating of the mask during writing.

In the 2000’s, resolution enhancement techniques (RET) and optical proximity correction (OPC), introduced in the 1990s, became increasingly complex. Today, the pattern on an inverse lithography technique (ILT) mask bears no resemblance to the pattern printed on the wafer and the mask has become a diffractive optical element, altering the intensity, phase, polarization, and direction of the light going through it. Simply inspecting the pattern on the mask using existing tools is no longer a good predictor of whether the mask is defect free, and aerial image-based inspection, where the inspection tool emulates a lithography scanner to make this judgement, became a necessity.

Abboud explained that the amount of data required to write each mask and the total number of masks has increased, creating productivity challenges as each mask can take over two days to write vs. the old norm of less than a half day. Abboud shared that in 2012 Intel and the industry predicted this growing data volume and maskmaking productivity challenge. The mask industry had also consolidated due to high capital costs and the benefits of mask/wafer co-optimization. This combined with the realization that slower photoresists produced better pattern fidelity, drove the need for development of multibeam mask writing (MBMW) and creation of the MBMW Consortium with industry partners, which enabled IMS to develop and be first to market with MBMW capability. This has returned mask write times to the half-day norm even when using slow, high resolution resist.

Abboud finished his talk by explaining the impact of the transition to EUVL on maskmaking, stating that EUVL masks will be ready and able to continue to extend Moore’s Law. He explained that EUV masks do the same job as optical masks, although making EUV masks impacts many of the process steps in the mask shop, starting at film on the bottom of the mask blank up through the final pellicle inspection. Mask equipment and blank suppliers have developed novel tools and materials to enable this transition with the help of industry consortia. Even with these broad changes, Intel’s mask shop is shipping masks to meet our development needs, and EUV masks are making progress toward achieving the goal of zero printable defects. In closing, Abboud stated that mask innovations will continue to enable the extension of Moore’s Law and future semiconductor industry growth, and the five decade long trend will continue.

Janice Golda is director of Lithography Strategic Sourcing in the Technology and Manufacturing Group at Intel.



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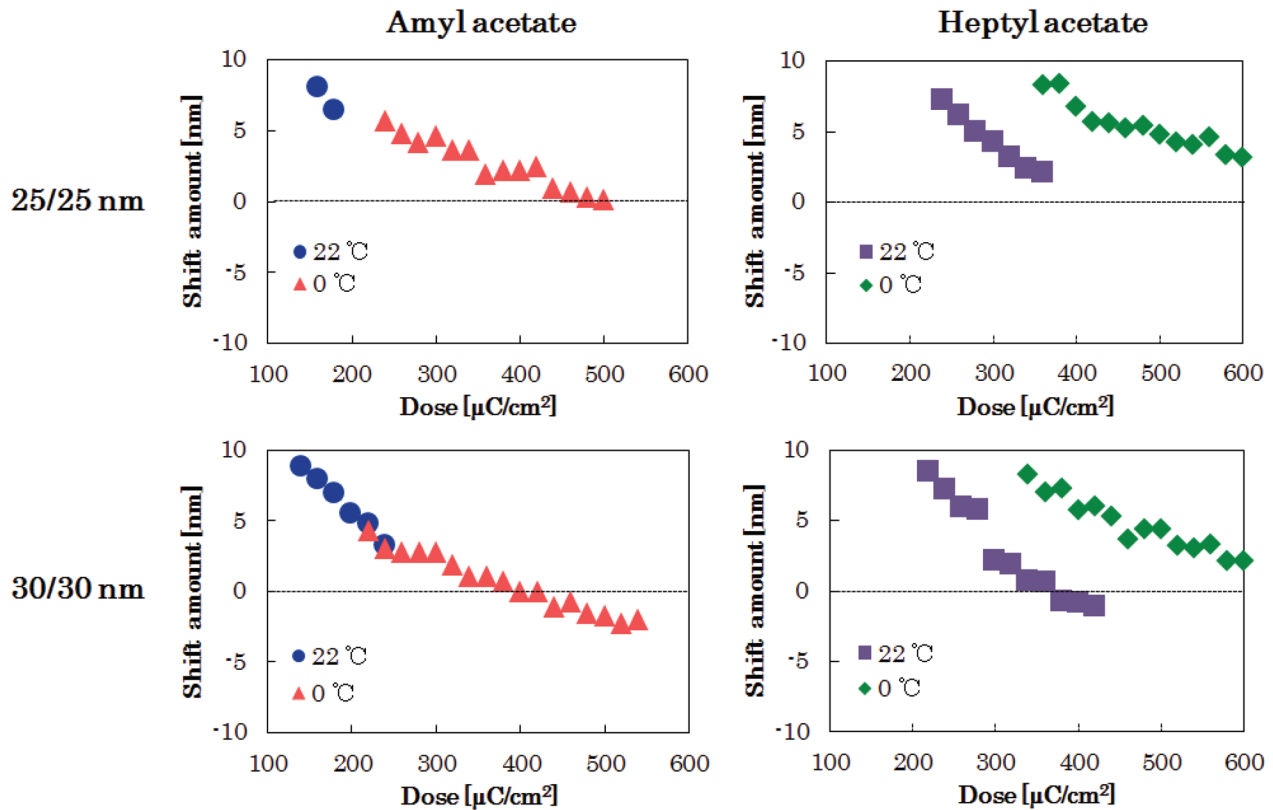


Figure 2. Exposure dose dependences of shift amount for 25/25nm and 30/30nm L/S patterns developed in amyl and heptyl acetates at 0°C and 22°C.

In addition, a semi dense pattern below 20nm is also needed. Non-chemically amplified (Non-CA) resists have good resolution compared to the chemically amplified (CA) resists, though the sensitivity is lower. Therefore, the polymer resist is expected as an electron beam resist for next generation photomask fabrication as well as a CA resist and a molecular resist. The performance of a polymer resist is mainly characterized by its chemical structure and molecular weight (Mw).<sup>[1-4]</sup> We have reported that the thickness loss in the unexposed portions of the resist in the 20nm L/S pattern is suppressed by increasing the molecular weight of the polymer resist consisting of methyl  $\alpha$ -chloroacrylate and  $\alpha$ -methylstyrene upto the Mw of 500 k.<sup>[1]</sup> With this structure, the resist possesses higher sensitivity and higher dry-etching resistance compared to poly-(methyl methacrylate) (PMMA) due to the existence of halogen unit and benzene ring.

Exposure characteristics of the resist are also strongly dependent on the development process conditions such as a developer, developing time and temperature.<sup>[5-7]</sup> It was reported that the sensitivity curves of ZEP520 resist developed in various ester solvents from xylene to octyl acetate indicated the higher contrast with increasing molecular size of developer, although the sensitivity became lower.<sup>[1]</sup> We have confirmed that the pattern shape became better when the developer molecular size was larger, for all the resists having the Mw's from 60 k to 500 k.<sup>[7]</sup> We also mentioned that the dissolution in the unexposed portions was suppressed, resulting that the dose margin of pattern formation, particularly in the case of the 60k-Mw resist, became wider with increasing developer molecular size. Cold development also enhanced the contrast of the chain-scission-

based resists such as PMMA and ZEP though the higher electron dose and longer development time are needed due to their lower dissolution rate.<sup>[8,11]</sup> It was explained that cold development has the effect of "freezing out" the polymer chains that have been partially exposed at the edges of a feature due to scattering of the electron beam.

Recently, Miyoshi and Taniguchi have demonstrated that the post exposure baking (PEB) process in the non-CA resist was effective as an advanced fabrication technique for high resolutions of the order of 20nm.<sup>[12]</sup> It was suggested that the space critical dimension (CD) of 1:1 L/S pattern and isolated space pattern were shrunk by increasing PEB temperature, though the resist sensitivity became gradually lower by increasing PEB temperature. They mentioned that the use of PEB with non-CA resist might have the possibility to help suppress the proximity effect and cause an annealing effect.

The above mentioned methods are effective to enhance the high-resolution capability but degrade the sensitivity. In this study, in order to form sub 20nm dense patterns of acrylic polymer type electron beam resist, we examine exposure characteristics of the polymer resist consisting of methyl  $\alpha$ -chloroacrylate and  $\alpha$ -methylstyrene with the average molecular weight of 500 k by changing the developer and development temperature. The effect of PEB on exposure characteristics is also investigated.

## 2. Experiments

The copolymer was synthesized by radical polymerization of methyl  $\alpha$ -chloroacrylate and  $\alpha$ -methylstyrene, and reprecipitation method was conducted.<sup>[13]</sup> The average Mw of the copoly-

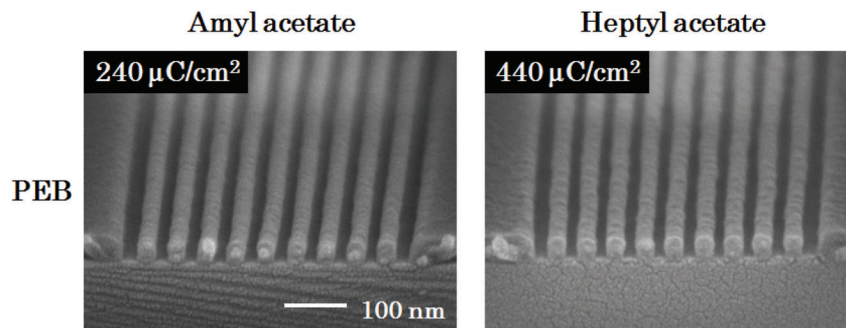


Figure 3. SEM images of 25/25nm L/S pattern with PEB developed in amyl and heptyl acetates at 22°C.

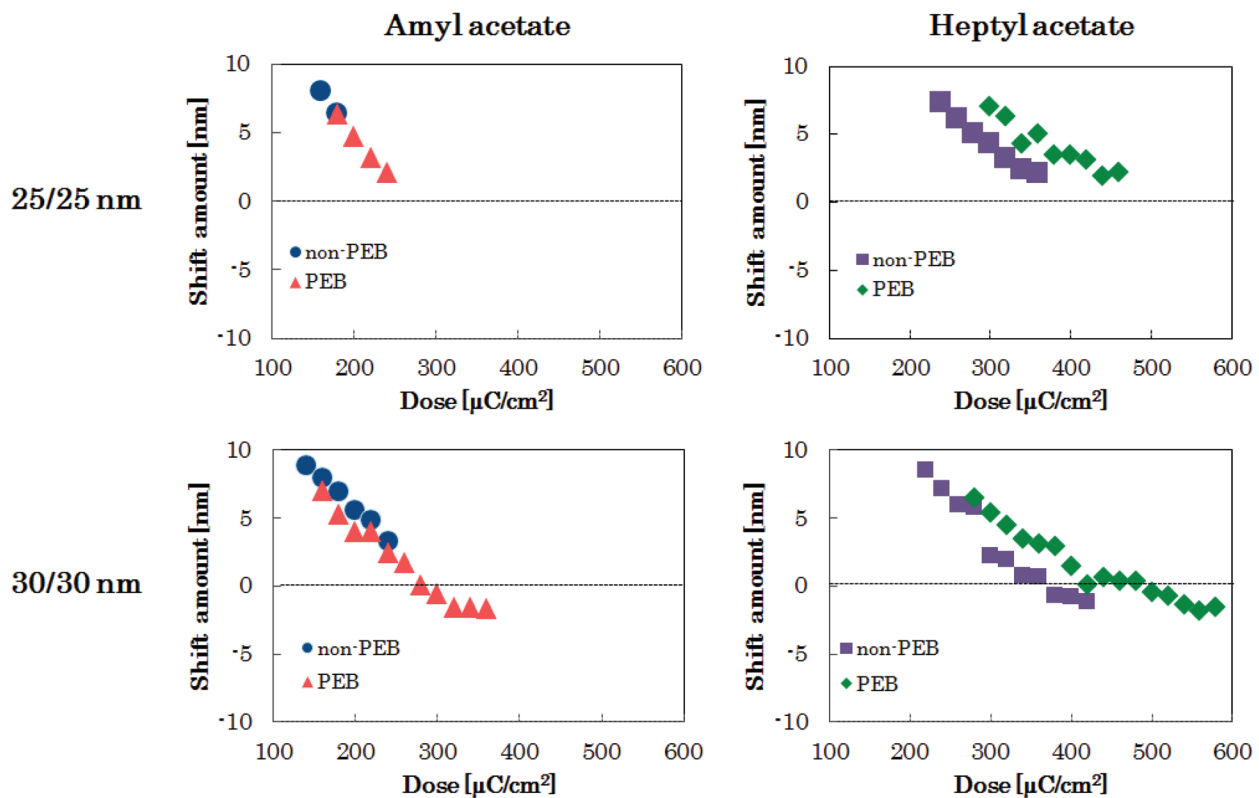


Figure 4. Exposure dose dependences of shift amount for 25/25nm and 30/30nm L/S patterns with and without PEB developed in amyl and heptyl acetates.

mer was characterized by size exclusion chromatography. The copolymer having the Mw of 500 k was dissolved in anisole (boiling point: 154°C). The resists having the thickness of approximately 30 and 45nm were spin-coated on a Si substrate by changing the rotation speed of coater. After pre-baking on a hot plate at 180°C for 2 min, exposure experiments were carried out using the electron beam writing system, ELS-7500EX (ELIONIX), with an acceleration voltage of 50 kV. The exposed line number of the L/S patterns was 10. A beam current was set to be 25 pA and the beam diameter was 3.2nm under the experimental conditions in this study. The field size of electron beam writing was 150Å~150 μm<sup>2</sup>, which consisted of 60000Å~60000 dots. Exposed samples were developed in amyl and heptyl acetates at 22°C for 60 s, and at 0°C for 120 s considering the lower dissolution rate in cold development. The resist pattern shape

observation was conducted by a scanning electron microscope (SEM).

### 3. Results and Discussion

25/25nm and 30/30nm L/S patterns (design value) were formed in the 45nm thick resists by changing the exposure dose upto 600 μC/cm<sup>2</sup> with the dose increment by 20 μC/cm<sup>2</sup> to examine the development process. Figure 1 shows the SEM images of the 25/25nm L/S pattern developed in amyl at 22°C, amyl at 0°C, heptyl at 22°C and heptyl at 0°C. The 0°C development patterns show the better shapes having the vertical sidewalls compared with the respective 22°C development patterns. The effect is remarkable in amyl acetate developer. The shift amount of the pattern width from the design value was measured from the

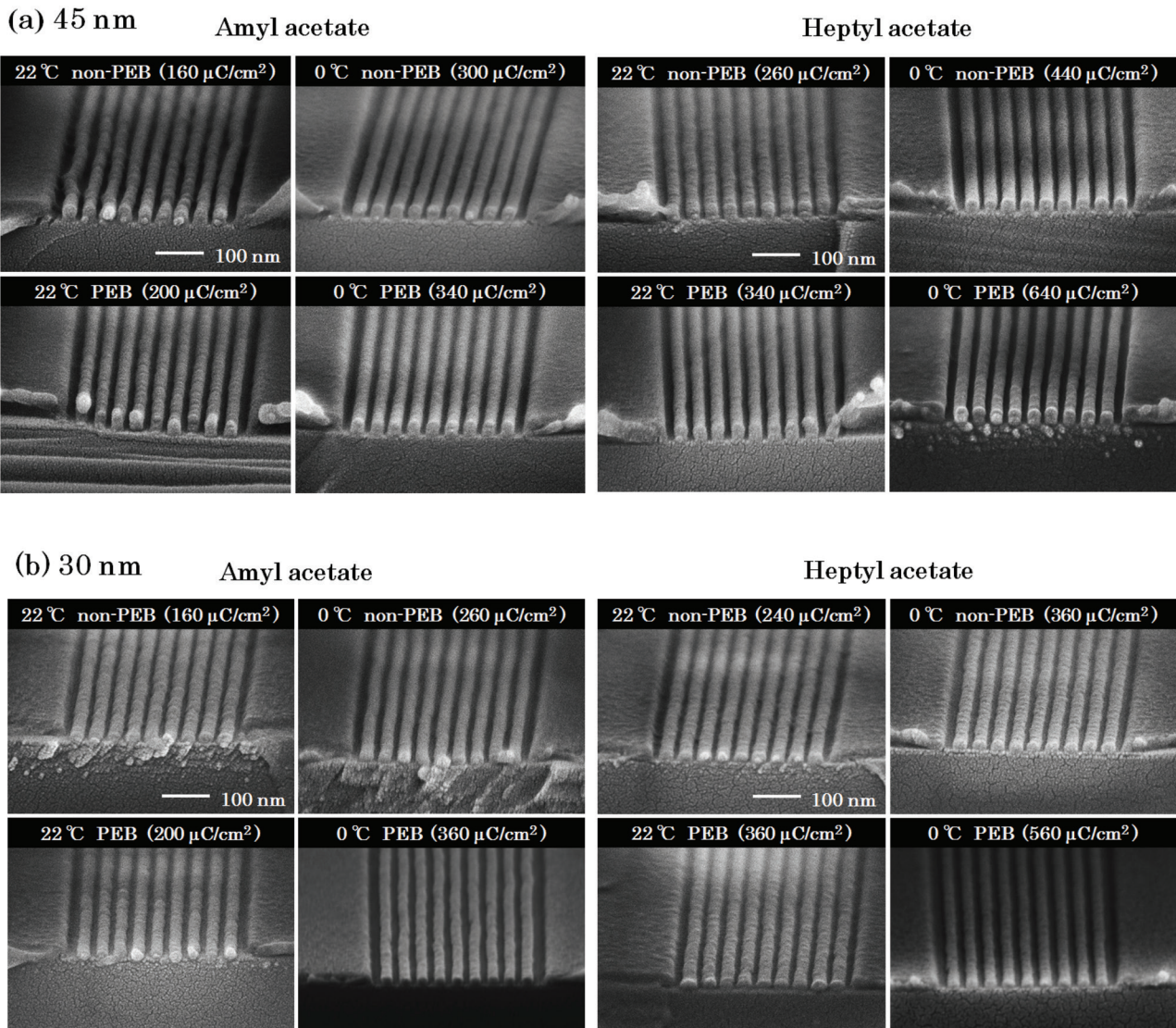


Figure 5. SEM images of 20/20nm L/S pattern fabricated by using PEB and/or 0°C development for amyl and heptyl acetates. The resist thicknesses are (a) 45nm and (b) 30nm.

top-view SEM images. Figure 2 shows the exposure dose dependence in the shift amount for the 25/25nm and 30/30nm L/S patterns developed in amyl and heptyl acetates at 0°C and 22°C. As shown in the figures, although the sensitivity becomes lower, the dose margins of pattern formation for 0°C development are wider than those for 22°C development. In particular, reduction of pattern width caused by the increase of the exposure dose is extremely small when the resist is developed in heptyl acetate at 0°C, and both the 25/25nm and 30/30nm L/S patterns still form until the maximum dose of 600  $\mu\text{C}/\text{cm}^2$  in this experiment. We also examined the exposure dose dependence of the shift amount of the pattern width by forming the 25/25nm L/S pattern in the 30nm thick resist and obtained the same tendency. The average minimum exposure doses required for the pattern formation, that is sensitivity, at 0°C development are increased by approximately 50% for both amyl and heptyl acetates compared with those at 22°C development, respectively, though the dose increment is 20  $\mu\text{C}/\text{cm}^2$  in this experiment.

Next, we examined the effect of PEB on exposure characteristics of the resist patterns with the design values of the 25/25nm and 30/30nm L/S. After the exposure, PEB was conducted using a hot plate at 120°C for 2 min. Figure 3 shows the SEM images of the 25/25nm L/S pattern with PEB developed in amyl and heptyl acetates at 22°C. The thickness of the resist is 45nm. For amyl acetate, the pattern shape is improved by PEB. The exposure dose dependences in the shift amount of pattern width for the 25/25nm and 30/30nm L/S patterns with and without PEB developed in amyl and heptyl acetates are shown in Fig. 4. Adding PEB process, the dose margin also becomes wider, although the sensitivity is lower. The average minimum exposure dose increment required for the pattern formation with PEB are 20% for amyl acetate and 30% for heptyl acetate. Miyoshi and Taniguchi reported that PEB effects became larger with increasing the PEB temperature. Further experiments are required to optimize PEB process such as baking temperature and time.

Figure 5 shows the SEM images of the 20/20nm L/S patterns

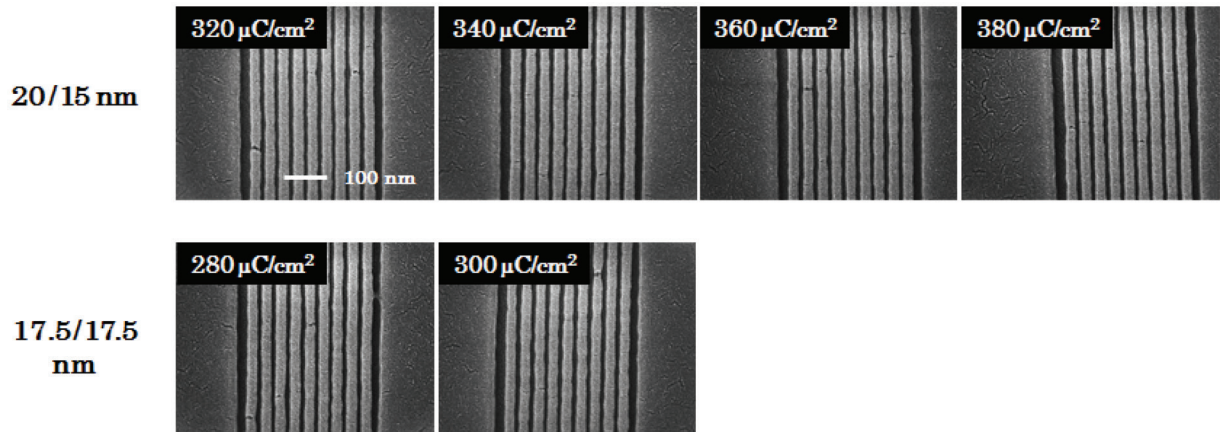


Figure 6. SEM images of 35nm pitch patterns with design values of 17.5/17.5nm and 20(unexposed region)/15(exposed region)nm L/S.0.

(design value) fabricated by using PEB and/or 0°C development for amyl and heptyl acetates. The resist thicknesses are (a) 45nm and (b) 30nm. The shape of the resist pattern with PEB or developed at 0°C, especially in amyl acetate, is better than that developed at 22°C without PEB.

Though the required exposure dose is even larger, the resist pattern is slightly improved by the combination of PEB and 0°C development. The effects of PEB and 0°C development with heptyl acetate on the 20/20 L/S pattern shape are weaker compared to those with amyl acetate, while the increment of the exposure dose required for the pattern formation with heptyl acetate is larger.

35nm pitch patterns with design values of 17.5/17.5nm and 20(unexposed region)/15(exposed region)nm L/S are fabricated and shown in Fig. 6. The thickness of the resist is 45nm. The exposed patterns are developed in amyl acetate at 0°C without PEB. The 35nm pitch patterns are successfully resolved from 320 to 380  $\mu\text{C}/\text{cm}^2$  for 20/15nm L/S and from 280 to 300  $\mu\text{C}/\text{cm}^2$  for 17.5/17.5nm L/S.

#### 4. Conclusions

We have examined the fabrication process of L/S patterns in the non-CA positive tone electron beam resist: a developer, development temperature and PEB. In the 25/25nm and 30/30nm L/S patterns, it is confirmed that 0°C development and PEB with the temperature of 120°C for 2 min are both effective to improve the pattern shape and dose margin, although the sensitivities are lower. The 20/20nm L/S patterns are fabricated by using PEB and/or 0°C development and the pattern shape is improved by PEB and/or 0°C development. The effects of PEB and 0°C development with heptyl acetate on the 20/20 L/S pattern shape are weaker compared to those with amyl acetate, while the increment of the exposure dose required for the pattern formation with heptyl acetate is larger. In the 45nm thick resist, 35nm pitch patterns are successfully resolved from 320 to 380  $\mu\text{C}/\text{cm}^2$  for 20/15nm L/S and from 280 to 300  $\mu\text{C}/\text{cm}^2$  for 17.5/17.5nm L/S by developing in amyl acetate at 0°C without PEB.

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# Industry Briefs

## ■ SEMI Reports 2016 Semiconductor Photomask Sales of \$3.3 Billion

April 10, 2017

SEMI, the global industry association representing the electronics manufacturing supply chain, announced that the worldwide semiconductor photomask market was \$3.32 billion in 2016 and is forecasted to reach \$3.57 billion in 2018. After increasing 1 percent in 2015, the photomask market increased 2 percent in 2016. The mask market is expected to grow 4 and 3 percent in 2017 and 2018, respectively, according to the SEMI report. Key drivers in this market continue to be advanced technology feature sizes (less than 45nm) and increased manufacturing in Asia-Pacific. Taiwan remains the largest photomask regional market for the sixth year in a row and is expected to be the largest market for the duration of the forecast. Revenues of \$3.32 billion place photomasks at 13 percent of the total wafer fabrication materials market, behind silicon and semiconductor gases. By comparison, SEMI reports that photomasks represented 18 percent of the total wafer fabrication materials market in 2003. Another trend highlighted in the report is the increasing importance of captive mask shops. Captive mask shops, aided by intense capital expenditures in 2011 and 2012 continue to gain market share at merchant suppliers' expense. Captive mask suppliers accounted for 63 percent of the total photomask market last year, up from 56 percent in 2015. Captive mask shops represented 31 percent of the photomask market in 2003.

<http://www.semi.org/en/semi-reports-2016-semiconductor-photomask-sales-33-billion>

## ■ Photomask Japan 2017

The 24<sup>th</sup> annual Photomask Japan symposium was held April 5-7, 2017 in Yokohama Japan. Total attendance was up 10% while submitted papers was about the same compared to 2016. Major topics included half-day sessions on Flat Panel Display Photomasks and GPU applications for Photomask data processing. Next year's conference will be held April 18-20, 2018 in Yokohama, Japan. Abstracts are due November 30, 2017.

## ■ EUV Litho Coming Into Commercial Focus

April 20, 2017

ASML expects to ship 20 to 24 extreme ultraviolet (EUV) lithography tools next year with an order backlog of 21 NXE:3400B EUV systems as the industry continues edging closer to production deployment of the oft-delayed next-generation lithography technology. ASML continues to make progress toward its goals of 125 wafers per hour productivity and 90 percent light-source availability. ASML stated that while there is still work to be done on things like the pellicle, there appear to be no major roadblocks for EUV insertion in the timeframes as indicated by customers. EUV is now poised to be deployed in production in the next couple years beginning with the 7nm node.

[http://www.eetimes.com/document.asp?doc\\_id=1331623](http://www.eetimes.com/document.asp?doc_id=1331623)

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Founded in 1980 by a group of chrome blank users wanting a single voice to interact with suppliers, BACUS has grown to become the largest and most widely known forum for the exchange of technical information of interest to photomask and reticle makers. BACUS joined SPIE in January of 1991 to expand the exchange of information with mask makers around the world.

The group sponsors an informative monthly meeting and newsletter, BACUS News. The BACUS annual Photomask Technology Symposium covers photomask technology, photomask processes, lithography, materials and resists, phase shift masks, inspection and repair, metrology, and quality and manufacturing management.

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11-14 September 2017  
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[www.spie.org/puv](http://www.spie.org/puv)

- ✱ **The 33rd European Mask and Lithography Conference EMLC 2017**  
27-29 June 2017  
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### 2018

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25 February-1 March 2018  
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