Fabricating a high-resolution mask with improved line-edge roughness by using a nonchemically amplified resist and a postexposure bake

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The authors have developed a high-resolution technique for fabricating photomasks at the 10-nm half-pitch logic nodes and beyond. Current mask-manufacturing techniques use a chemically amplified resist (CAR) that has a complex mechanism of acid generation, complicating the criteria for selecting the polymer and the quencher for industrial purposes. Thus, it is important to study fabricating masks with non-CARs. The authors exposed a non-CAR, diluted ZEP520A, to variable-shaped electron-beam lithography and used a postexposure bake (PEB) to modify the resist. Studying how the PEB temperature affected the non-CAR and resultant masks, the authors demonstrate that their technique can produce high-resolution structures. By measuring the critical dimensions (CDs), the authors show that the PEB shrunk, enlarged, and retained the size of 1:1 line-and-space, isolated space, and isolated line patterns, respectively. By optimizing the PEB temperature, the authors improved the line-edge roughness (LER) of the 1:1 line-and-space and isolated space CDs by ~40%. To understand how the PEB affected the resultant structures, the authors measured the hardness of cured resists with and without a PEB at various temperatures. Optimizing the PEB temperature of the non-CAR increased the resist contrast, annealing the resist and improving the LER. As such, their technique is capable of high resolutions on the order of 20 nm. The insights the authors gained from optimizing the PEB might be useful when fabricating next-generation masks. © 2015 American Vacuum Society.

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I. INTRODUCTION

The trend in scaling of integrated circuits known as Moore's law¹ is likely to continue in the forthcoming 10- and 7-nm nodes. The latest edition of the *International Technology Roadmap for Semiconductors* (ITRS)² set out challenging requirements for 10-nm half-pitch logic nodes in terms of sub-resolution feature sizes for photomasks, and it calls for high resolutions on the order of 40 nm. Developing next-generation masks will likely require even finer resolutions.

Currently, masks are normally manufactured by using chemically amplified resists (CARs). To pattern these resists, a photochemical acid generator (PAG) produces an acid, which dissolves the resist in a controlled manner through catalytic reactions. This process enables high sensitivity and high resolution. However, there are concerns regarding post-coating delay stability, postexposure delay stability, and other effects resulting from the use of the CAR material itself, including the complex mechanism of acid generation;³ these factors complicate the criteria for selecting the polymer and the quencher for industrial purposes. Furthermore, these patterned resists have issues related to surface roughness, referred to as line-edge roughness (LER) or line-width roughness. Understanding LER is important for designing materials and processes, and the causes of LER have been

intensively investigated over the past 20 years.^{4,5} Consequently, to best decide on and develop more-robust acceptance criteria for alternatives to manufacturing existing CAR-based masks, it is important to carefully evaluate non-CAR photoresists that do not contain PAGs.

In the present work, we fabricated high-resolution masks by using variable-shaped electron-beam (VSB) lithography (JBX9000, JEOL, Ltd., Tokyo, Japan) with ZEP520A (Ref. 6) (Zeon Corporation, Tokyo, Japan), a positive electron-beam non-CAR. As part of our ongoing efforts to develop high-resolution fabrication techniques, we also studied the use of a postexposure bake (PEB), a process known to anneal spin-coated films on glass.⁷ Typically, a PEB is used to increase the sensitivity of CARs. In contrast, here we fabricated a mask with a non-CAR and a PEB, demonstrating that this is a feasible high-resolution technique. To investigate how the PEB improved the resolution and LER, we examined the contrast curve of the resist and characterized its curing process by using a dynamic ultramicrohardness tester. Annealing is necessary to transform the non-CAR material by hardening its structure.⁸ However, when a polymer is annealed, its microhardness changes with the annealing temperature.^{8,9}

II. EXPERIMENTAL SETUP AND METHODOLOGY

Quartz substrates coated with a 60-nm-thick layer of chromium were used as mask blanks. ZEP520A diluted 1:1 with ZEP-A thinner [98% methoxybenzene (anisole)] was

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FIG. 1. Top-down SEM images showing the PEB temperature dependences for LS, IS, and IL patterns (design CD: 100 nm; magnification: 75 000 $\times$).

used as a non-CAR sample. Dilution is necessary to produce thin films of the resist to prevent pattern collapse. The diluted resists were spin-coated (CTS8000, Sigmameltec, Ltd., Kanagawa) onto the mask blanks at 1500 rpm for 2 s during drop casting and then at 1000 rpm for 60 s, producing a film thickness of less than 50 nm. The resists were then baked at 180 °C for 600 s in an oven on the same tool.

After spin-coating and curing, the resists were exposed to electron-beam lithography (EBL; JBX9000 50-kV EBL, JEOL, Ltd.). The tool we used is the most advanced commercially available 6-in. mask-writing variable-shaped beam tool, and its performance has been thoroughly assessed with various types of resist, permitting us to fully exploit its advanced

proximity-effect correction and carefully optimize the lithography process.^{10–12} We used a mask pattern layout with eight regions, including a 1:1 line-and-space (LS) pattern, an isolated space (IS) pattern, and an isolated line (IL) pattern.¹³ Once the EBL process had been completed, several masks were processed for validation of the PEB process, which was performed at a temperature of 90, 120, 135, or 150 °C for 60 s in an oven.

After the PEB, the resists were developed by soaking in ZED-N50 (>99% pentyl acetate; Zeon Chemicals L.P., Louisville, KY) for 80 s at room temperature (20–23 °C). The samples were then rinsed in 9% propan-2-ol for 20 s and dried.

FIG. 2. (Color online) Design CD 100 nm resist sensitivity curve for IL, LS, and IS patterns at various PEB temperatures.

FIG. 3. Cross-sectional SEM images showing values of the LER for various PEB temperatures (design CD: 100 nm).

To determine the variations in critical dimensions (CDs), we used a CD scanning electron microscope for photomask applications (LWM9000; Leica Microsystems GmbH, Wetzlar).¹⁴ This microscope has proprietary electron optics and an improved detection system, almost completely eliminating issues associated with charging and contamination, allowing for repeatable subnanometric measurements of CDs. We examined the repeatability and reproducibility of the CD measurements by measuring at five different locations for each pattern size (designed CDs: 100, 70, 50, 44, 40 nm or lower measurable pattern size) for the LS, IS, and IL patterns. The measurements were performed at a beam energy of 500 eV with a probe current of -4.8 pA. The SEM magnification was usually $200\,000\times$, but we used $75\,000\times$ when required.

To investigate the LER improvement, we examined the contrast curve of the resist. We used a specific mask layout to measure the film thickness and resist dissolution rate. Measurements were performed at 24 locations (one site = 0.35×0.35 in.) on each mask blank. To produce the contrast curve, we applied random doses of 0 – $300 \mu\text{C}/\text{cm}^2$ to the various measurement sites and then measured the thicknesses of the resultant films after the PEB and development.

We also examined the PEB process to determine how it enabled such a high resolution. Using a dynamic ultramicrohardness tester, we studied how the PEB affected the hardness of samples with and without exposure to the electron beam. We prepared four samples: two samples were exposed to the electron beam, and two were left unexposed; one exposed sample and one unexposed sample were subjected to the PEB at 120°C for 20 min. The four samples had a coupon size of 1.8×1.8 mm. The samples for these tests were exposed to EBL in an ESA-2000 ELIONIX tool at an accelerating voltage of 10 kV and beam current of 900 pA, giving $50 \mu\text{C}/\text{cm}^2$. These samples were then subjected to a fixed load in a microhardness tester (DUH-211, Shimadzu Corp.,

Kyoto), and we determined their average hardness from three such loading–unloading tests.

III. RESULTS AND DISCUSSION

A. Dependence of the critical dimensions on the postexposure bake and resist sensitivity

Figure 1 shows top-down SEM images of the LS pattern ($164 \mu\text{C}/\text{cm}^2$), IS pattern ($239 \mu\text{C}/\text{cm}^2$), and IL pattern ($126 \mu\text{C}/\text{cm}^2$), showing how they changed with the PEB temperature. For the 1:1 LS pattern, there was no significant difference between the CDs of samples subjected to a PEB at 90°C and those of samples not subjected to a PEB. However, the space CD shrank gradually as the PEB temperature increased from 90 to 135°C and then contracted markedly at 150°C . These results suggest that the space CD of the 1:1 LS pattern shrank because of the increasing PEB temperature.

Similarly, the IS pattern shrank with increasing PEB temperature; at 150°C , it contracted by $\sim 28\%$ (measured CD of 79 nm) compared with the non-PEB sample (measured CD of 110 nm). Conversely, the IL pattern expanded with increasing PEB temperature. The line widths for the non-PEB sample and the sample subjected to a PEB at 90°C were almost identical; however, the line width slightly expanded at a greater PEB temperature of 120°C , and it increased markedly at an

TABLE I. LS, IS, and IL adaptive doses for various PEB temperatures (units: $\mu\text{C}/\text{cm}^2$).

	Non-PEB	PEB 90°C	PEB 120°C	PEB 135°C	PEB 150°C
LS	150	154	157	167	171
IS	222	224	227	242	271
IL	111	113	116	124	130

Fig. 4. (Color online) Summary of improvements in the LER [design CD: (a) 100 nm and (b) 50 nm, Error bar: 95% confidence interval].

even greater PEB temperature of 150 °C. We assume that these changes occurred because the increase in PEB temperature decreased the resist sensitivity, attenuating the effect of electron-beam exposure.

Figure 2 shows the resist sensitivity curves for IL, LS, and IS patterns at a design CD of 100 nm. The CD error from the target value for the IL pattern was converted into a space CD (the designed CD minus the measured line width), while the errors for the LS and IS patterns were calculated as the measured space CD minus the designed CD. As the PEB temperature increased, the resist sensitivity of every patterned structure (LS, IS, and IL) gradually decreased. At a PEB temperature of 120 °C, the space CD shrinkage and line-width expansion were marked, and an even higher PEB temperature of 150 °C produced a resist with extremely low sensitivity. The resist sensitivity for the 1:1 LS pattern was 150 $\mu\text{C}/\text{cm}^2$ for the non-PEB sample, 154 $\mu\text{C}/\text{cm}^2$ for the PEB 90 °C sample, 157 $\mu\text{C}/\text{cm}^2$ for the PEB 120 °C sample, 167 $\mu\text{C}/\text{cm}^2$ for the PEB 135 °C sample, and 171 $\mu\text{C}/\text{cm}^2$ for the PEB 150 °C sample. The IS and IL patterns showed similar trends in sensitivity (Table I). These results demonstrate that the resist sensitivity depended on the PEB temperature.

B. Investigation for the line-edge roughness

Figure 3 shows cross-sectional SEM images of the LS, IS, and IL patterns, showing how they changed with PEB temperature at the relevant optimal dose, based on sensitivity optimization (Table I). We measured the LER from a 100-nm pitch on the LS pattern, and we calculated the three-sigma value for each line. For non-PEB samples, the LERs for the LS, IS, and IL patterns were 8.7, 7.1, and 8.9 nm, respectively. As the PEB temperature increased up to 120 °C, the LER decreased gradually; at 120 °C, the LERs for the LS, IS, and IL patterns were 5.1, 4.4, and 6.6 nm, respectively. As the PEB temperature increased further to 135 and 150 °C, however, the LER deteriorated. Thus, a PEB temperature of 120 °C appears to be optimal for improving the LER.

Figure 4 summarizes data pertaining to LER improvement for designed CD values of 100 and 50 nm for the LS, IS, and IL patterns at the optimal dose. This figure shows that the optimal PEB temperature for minimizing the LER is 120 °C.

To improve the LER, we also investigated the contrast curve of the resist (Fig. 5). The sample with a PEB at 150 °C

had a contrast curve that changed gently (gamma value: 2.9) and was less sensitive to the development dose than for those of samples without a PEB and with a PEB at 120 °C. For the sample with a PEB at 120 °C, its contrast curve was sharper (gamma value: 12.8) than that of the non-PEB sample (gamma value: 7.2), and its LER decreased.

C. Resolution capability

Figure 6 shows cross-sectional SEM images for the best resolution with a PEB 120 °C for each of the pattern structures. The LS and IS resolutions reached 28 and 22 nm, respectively. An IL resolution of 31 nm was achieved. These results show that, with an optimized PEB temperature, our technique can produce high resolutions on the order of 20 nm. For limitations on the resolution capability with respect to changes in various CDs with and without a PEB, see our recent report.¹³

D. Discussion of the enhanced resolution and LER

Figure 7 shows the chemical structures of ZEP520A and PMMA.¹⁵ ZEP520A resist is a classical chain-scission-type positive resist, the same type as PMMA, because electron-beam exposure causes chain-scission of both homopolymers, alpha-chloromethacrylate and alpha-methylstyrene, and chemical crosslinking.¹⁶

ZEP520A must be baked to evaporate the organic solvent remaining in the resist after spin-coating. If it is baked at a too low temperature or for a too short time, the resist retains a granular structure,^{17,18} which has high surface roughness.

Fig. 5. (Color online) ZEP520A contrast curve with no PEB and with a PEB at 120 or 150 °C.

FIG. 6. High-resolution capability for diluted ZEP520A with a PEB at 120 °C.

FIG. 7. (Left) PMMA and (right) ZEP520A polymer structures.

When polymer molecules have enough time to diffuse into the resist by baking at the optimum temperature, the resultant film will have lower surface roughness because the granular structure would have been smoothed.^{17,18} To reduce the surface roughness of the granular structure, the resist must be baked at its glass-transition temperature or higher; for ZEP520A, this temperature is 105 °C.⁶

When a positive-tone chain-scission-type resist, such as ZEP520A or PMMA, is exposed to an electron beam, its main-chain C–C bonds break in response to impacts of

FIG. 8. (Color online) Results of dynamic ultramicrohardness testing of exposed and nonexposed areas of samples with no PEB and with a PEB at 120 °C.

FIG. 9. Cross-sectional SEM images showing IS samples (design CD: 100 nm) with no PEB and with a PEB at 120 or 150 °C.

primary and secondary electrons as well as electrons back-scattered from the substrate.^{15,16} This chain-scission reduces the molecular weight of the resist, eventually producing the granular structure.^{18,19} The resist should develop from the granular units. In this case, it causes the resist to develop unevenly, worsening its resolution.^{17,18}

Some parts of the exposed film with the granular structure can be smoothed by a PEB.^{17,18} The PEB would return the granular structure, generated by chain-scission during exposure, to its state prior to exposure, preventing it from dissolving in the developer.^{17,18} Our optimized PEB temperature (120 °C) is higher than the reported glass-transition temperature of ZEP520A, and baking at 120 °C smoothed the surface of the resist.⁶ We assume that the glass-transition temperature of ZEP520A after exposure is higher than the reported temperature because we baked the spin-coated resist at 180 °C for 10 min before exposure. A high-temperature bake (>200 °C) can suppress the granular structure, but this causes thinning of the resist.¹⁷ We believe that our film smoothed because we found no evidence of resist thinning.

In chain-scission-type resists, secondary electron scattering has been reported to be 10–50 nm vertically and 10–20 nm horizontally at 10–60 keV (100–540 $\mu\text{C}/\text{cm}^2$).^{15,20} Ritsko *et al.* explored electron-beam damage of these resists through chain-scission at energies below 1 keV,²¹ concluding that, to prevent damage, the resist should be exposed to secondary electrons with low energy. Furthermore, Bermudez studied how low-energy electron irradiation (10–50 eV) affected thin films of resist.²⁰ Because this energy range falls within the area of low-energy chain-scission (several tens of electron volt to ~ 1 keV), we believe that a PEB should reform a smooth film, and it does not mean that all the exposed area affected by the PEB would not dissolve in the developer. The area exposed to the primary electron beam at high energy should dissolve, while the area exposed to low-energy secondary electrons would recover during the PEB at an optimized temperature, producing a smooth film that will not dissolve in the developer. Consequently, we believe that it is possible to write an electron-beam pattern with the designed CD nearly equal to the writing area of the primary electron-beam exposure.

Overall, we believe the high resolution was enabled by resist annealing from the PEB.

The areas exposed to the electron beam should be soft because they are easily dissolved during development, and the nonexposed areas should be harder. To check this, we examined how the electron-beam exposure affected the hardness of samples with and without a PEB (Fig. 8). Figure 8 shows the results of microhardness tests at a fixed force in exposed and nonexposed areas with and without a PEB at 120 °C. The exposed area without a PEB at 120 °C was the softest, while the nonexposed area with a PEB was the hardest. It appears that the hardness of the resist is recovered by the PEB process. Figure 9 shows cross-sectional SEM images for the IS pattern samples without a PEB and with a PEB at 120 or 150 °C. The space for the sample with a PEB at 150 °C shrank more than 30 nm, and that of the sample with a PEB at 120 °C shrank by

6 nm. These results adequately demonstrate that the PEB annealed the exposed non-CAR film.

At a PEB temperature of 150 °C, the space edge roughness degraded to some extent, while at 120 °C the side wall of the space showed no significant degradation, similar to the sample without a PEB. This space shrinkage seems to show that the PEB makes part of the area exposed to the low-energy electron beam insensitive to development. At a PEB temperature of 150 °C, the space edge roughness was not finely shaped because of the marked tendency to undergo space shrinkage. Thus, a PEB temperature of 150 °C is too high.

LER is defined as the roughness measured from a top-down perspective on the edges of exposed lines, while surface roughness is measured from a scan of surface topography.^{17–19,22,23} Sidewall roughness is a particularly important subset of surface roughness because it is present on the vertical sidewalls of resist structures and thus directly affects LER. The surface roughness (side wall) comes from the size of the resist polymer molecules (molecular weight) and molecule aggregates. These granular aggregates determine the resolution of the resist and the quality of the resultant structures.¹⁹ Increasing the granularity, and thus increasing the surface roughness, increases the LER.^{17–19,22,23} By decreasing the surface roughness and thus the LER, a high resolution can be achieved.

Consequently, optimizing the PEB temperature might permit a high resolution at very small CDs, and controlling the PEB temperature might mitigate exposure effects such as secondary electron scattering.

IV. SUMMARY AND CONCLUSIONS

Using a non-CAR (ZEP520A) and a PEB with an optimized temperature helped to increase the contrast of the resist, annealing the resist and improving the LER; this result might lead to an advanced technique for fabricating patterns with high resolutions on the order of 20 nm.

As a part of ongoing efforts to achieve a high resolution with ZEP520A, research has been done on low-temperature development and alternative developers to produce resolutions below 30 nm or even below 20 nm.^{24–26} These resolutions could be achieved by using the optimized PEB found in this research and a low-temperature development process as the next step. Consequently, we believe that a resolution on the order of 20 nm, which we achieved in this work by using a VSB tool with a non-CAR and a PEB, might be useful in advanced methods for fabricating next-generation masks.

We showed that increasing the PEB temperature shrunk the LS and IS patterns and expanded the IL pattern, and we investigated how the resist sensitivity changed with PEB temperature. Effectively, using a non-CAR with a PEB should produce high-resolution patterns, while considering CD errors in the target. This process might reduce the productivity of mask fabrication because the lower sensitivity of the resist would increase the mask-writing time. However, mask-writing times are bound to increase markedly for conventional VSB mask-writers in future technology nodes because the

number of shots will increase exponentially while the exposure dose must increase simultaneously. Even so, we expect that mask-writing technology will improve dramatically through the use of multibeam mask writers.^{27–29}

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- ¹G. E. Moore, *Electronics* **38**, 114 (1965).
- ²ITRS, International Technology Roadmap for Semiconductors, “Table LITH4 optical requirements,” http://www.itrs.net/Links/2013ITRS/2013Tables/Litho_2013Tables.xlsx (accessed June 2015) (2013).
- ³J. F. Van Steenberg, N. Ootsuka, X. Buch, B. Icard, C. Sourd, C. Constancias, B. Dalzotto, and L. Pain, *Proc. SPIE* **8323**, 83232M (2012).
- ⁴H. Ito, *Proc. SPIE* **3678** (1999).
- ⁵R. A. Lawson and C. L. Henderson, *Microelectron. Eng.* **86**, 741 (2009).
- ⁶ZEON Corp., ZEP520A Technical Report, Version 2, <https://www.zeon-chemicals.com/pdfs/ZEP520A.pdf> (accessed June 2015) (2010).
- ⁷N. Unno, J. Taniguchi, M. Shizuno, and K. Ishikawa, *J. Vac. Sci. Technol. B* **26**, 2390 (2008).
- ⁸S. Warisawa, K. Kuroda, S. Chen, R. Kometani, and S. Ishihara, *J. Photopolym. Sci. Technol.* **25**, 37 (2012).
- ⁹H. Afifi and E. Hasan, *Polym.-Plast. Technol.* **42**, 543 (2003).
- ¹⁰T. Komagata, Y. Nakagawa, N. Gotoh, and K. Tanaka, *Proc. SPIE* **4343**, 736 (2001).
- ¹¹T. Komagata, Y. Nakagawa, N. Gotoh, and K. Tanaka, *Proc. SPIE* **4409**, 248 (2001).
- ¹²L. Raffaele, C. Pogliani, G. L. Cassol, G. Bianucci, S. Murai, S. Murata, R. Hikichi, H. Katsuki, and S. Noguchi, *Proc. SPIE* **5992**, 59924W (2005).
- ¹³H. Miyoshi and J. Taniguchi, *Microelectron. Eng.* **143**, 48 (2015).
- ¹⁴G. W. B. Schlueter, T. Nakamura, J. Matsumoto, M. Seyama, and J. M. Whittey, *Proc. SPIE* **5567**, 876 (2004).
- ¹⁵K. Koshelev, M. A. Mohammad, T. Fito, K. L. Westra, S. K. Dew, and M. Stepanova, *J. Vac. Sci. Technol. B* **29**, 06F306 (2011).
- ¹⁶T. Nishida, M. Notomi, R. Iga, and T. Tamamura, *Jpn. J. Appl. Phys.* **31**, 4508 (1992).
- ¹⁷N. Arjmandi, L. Lagage, and G. Borghs, *J. Vac. Sci. Technol. B* **27**, 1915 (2009).
- ¹⁸Y. M. Georgiev, W. Henschel, A. Fuchs, and H. Kurz, *Vacuum* **77**, 117 (2005).
- ¹⁹A. Gangnaik, Y. M. Georgiev, and J. D. Holmes, *J. Vac. Sci. Technol. B* **33**, 041601 (2015).
- ²⁰V. M. Bermudez, *J. Vac. Sci. Technol. B* **17**, 2512 (1999).
- ²¹J. J. Ritsko, L. J. Brillson, R. W. Bigelow, and T. J. Fabshi, *J. Chem. Phys.* **69**, 3931 (1978).
- ²²M. Aktary, M. Stepanova, and S. K. Dew, *J. Vac. Sci. Technol. B* **24**, 768 (2006).
- ²³H. Namatsu, M. Nagase, T. Yamaguchi, K. Yamazaki, and K. Kurihara, *J. Vac. Sci. Technol. B* **16**, 3315 (1998).
- ²⁴M. A. Mohammad, K. Koshelev, T. Fito, D. A. Z. Zheng, M. Stepanova, and S. Dew, *Jpn. J. Appl. Phys.* **51**, 06FC05 (2012).
- ²⁵H. Wang, G. M. Laws, S. Milicic, P. Boland, A. Handugan, M. Pratt, T. Eschrich, and S. Myhajlenko, *J. Vac. Sci. Technol. B* **25**, 102 (2007).
- ²⁶S. Long, Z. Li, X. Zhao, B. Chen, and M. Liu, *Proc. SPIE* **5645**, 255 (2005).
- ²⁷C. Klein, H. Loeschner, and E. Platzgummer, *Proc. SPIE* **8880**, 88801E (2013).
- ²⁸E. Platzgummer, C. Klein, and H. Loeschner, *J. Micro/Nanolithogr., MEM, MOEMS* **12**, 031108 (2013).
- ²⁹F. E. Abboud, M. Asturias, M. Chandramouli, and Y. Tezuka, *Proc. SPIE* **9235**, 92350W (2014).