Faculty and Staff Publication:

Nathaniel Cady, PhD

Version of Record

Citation for Final Published Published Work:

Desai, V., Mellish, M., Bennett, S., & **Cady, N. C.** (2017). Process development for high resolution hydrogen silsesquioxane patterning using a commercial scanner for extreme ultraviolet lithography. *Journal of Vacuum Science & Technology B, Nanotechnology and Microelectronics: Materials, Processing, Measurement, and Phenomena*, 35(2), 021603. doi: 10.1116/1.4975797

Link to Publisher's Site:

<http://avs.scitation.org/doi/10.1116/1.4975797>

DOI link:

<http://dx.doi.org/10.1116/1.4975797>

Process development for high resolution hydrogen silsesquioxane patterning using a commercial scanner for extreme ultraviolet lithography

Vishal Desai, Mac Mellish, Stephen Bennett, and Nathaniel C. Cady^{a)}

Colleges of Nanoscale science and Engineering (CNSE), SUNY Polytechnic Institute, 257 Fuller Road, Albany, New York 12203

(Received 22 November 2016; accepted 23 January 2017; published 9 February 2017)

The semiconductor industry is transitioning toward the use of extreme ultraviolet (EUV) lithography as a next generation patterning technology. There are currently only a limited number of high resolution EUV photoresists reported with EUV patterning capabilities, and those are generally tested using EUV-interference lithography. One such resist is the more commonly known electron beam resist, hydrogen silsesquioxane (HSQ), which is also sensitive to EUV exposure. In the present work, high resolution, dense, subdense patterning of HSQ resist on 300 mm wafers was demonstrated using ASML's NXE 3300B scanner. The critical dimensions analyzed ranged from 18 to 10 nm. Resolution down to 10.0 on 21.0 nm spacing was achieved with 6.5 nm line width roughness. This demonstration of high resolution EUV patterning of HSQ on a commercial scanner makes this process potentially viable for high volume manufacturing. © 2017 American Vacuum Society. [<http://dx.doi.org/10.1116/1.4975797>]

I. INTRODUCTION

Hydrogen silsesquioxane (HSQ) is primarily classified as a negative tone electron beam lithography (EBL) resist. High resolution patterning of HSQ (sub-10 nm) has been demonstrated using EBL;¹ however, the extremely low throughput of high resolution EBL systems prevents its use in high volume manufacturing (HVM). Previous reports have also shown that HSQ resist can be cross-linked with extreme ultraviolet (EUV) light.² HSQ resist has a cage like structure in which Si-H bonds are located at each corner and are bridged by oxygen atoms.³ After exposure with EBL or EUV, HSQ resist is converted into a material close in composition to silicon oxide.⁴ At this time, there are no reports in the literature that explain the exact mechanism by which HSQ responds to EUV light; however, the exposure mechanism of HSQ resist with the electron beams has been reported.^{5,6} During electron beam exposure, the Si-H bond of HSQ resist breaks, resulting in Si-O crosslinking and generation of water as a by-product.⁵ Another reported exposure mechanism suggests that after electron beam exposure, the HSQ experiences a redistribution reaction, which subsequently causes crosslinking via oxygen bridges between the HSQ molecules and generation of silane (SiH₄).⁶ In EUV exposure, high energy EUV photons get absorbed in the photoresist which then generates photoelectrons. These photoelectrons further experience scattering in the photoresist, generating secondary electrons, which can participate in resist exposure. Therefore, the mechanism of EUV exposure is considered to be closely related to the mechanisms previously explained for direct electron beam exposure.⁷

The higher etch resistance of patterned HSQ renders it similar to a so-called hard mask layer, and therefore provides greater flexibility of pattern transfer to variety of substrates, including Si. HSQ has lower sensitivity than other reported

EUV resists⁸ and hence requires a higher total dose to pattern. There have been several scientific papers reporting HSQ patterning with EUV-interference lithography (EUV-IL),⁹⁻¹² which is a low cost approach of creating aerial images that also provides infinite depth of focus. This process offers advantages in resist testing since it is relatively simple and does not have the same limitations typically found in projection optics.¹³ In previous work, ~20 nm half pitch HSQ lines were reported when using concentrated (2.6 N) tetramethylammonium hydroxide (TMAH) developer for 60 s.¹⁴ This suggests that while ~20 nm L/S HSQ patterns are achievable, the developer needs to be concentrated (2.6 N) for a short development process. Resolution down to 18 nm half pitch¹⁰ and sub-10 nm has been reported¹¹ using EUV-IL, as opposed to a commercial EUV scanner.

In the work presented here, we discuss the results of high resolution HSQ patterning using a commercial EUVL scanner (ASML NXE 3300B). Our foundry-based process was developed using a 300 mm wafer platform, with the focus on transition toward HVM. Further, the current study emphasizes development of a patterning scheme devoid of resist underlayers, to reduce process steps both at lithography and at pattern transfer.

II. EXPERIMENT

HSQ (XR-1541) from Dow Corning was used as the patterning resist for this work. Spin coating and development of HSQ resist was performed using a TEL LITHIUS PRO Z Track (Tokyo Electron, Corp.). Post-lithography, the CD-SEM measurements were performed using a Hitachi-CG5000. The instrument measures multiple (>10) positions along a feature and then provides average measurement data for both critical dimension (CD) and line width roughness (LWR). The cross section-SEM data were analyzed using Hitachi-4800 and Hitachi-5200 SEM instruments. Production grade 300 mm Si wafers were spin coated with a spin speed

^{a)}Electronic mail: ncady@sunypoly.edu

Fig. 1. (Color online) Schematic showing 10 nm line sets from the EUV reticle used in this work. Each different set of lines has a pitch varying from 1:1 to 1:5 L/S. The reticle contained patterns ranging from 28 to 10 nm.

of 2700 rpm to get ~ 35 nm of HSQ film thickness. Post-spin coating, the wafer received a post-applied bake of 200°C for 2 min. The reticle used for exposure has patterns ranging from 28 to 10 nm CD with pitches varying from 1:1 line/space (L/S) to 1:5 L/S. The patterns analyzed in the present work were in the range of 10–18 nm with L/S ranging from 1:1 to 1:3. For processing within the foundry production line, the TMAH developer concentration used was 0.26 N. As a result, the concentrated TMAH developer (2.6 N) and the other reported high resolution developers (e.g., salty developer¹⁵) were not used in this work. In Fig. 1, a schematic of the 10 nm patterns with varying pitches is shown for the purpose of depicting the photomask/reticle layout.

The ASML NXE 3300B scanner provides a production platform for EUVL and is a step and scan system which uses a $4\times$ reduction lens assembly. The numerical aperture (NA) is 0.33, and the 22 nm resolution (dense features) can be achieved using conventional illumination. Off-axis illumination further improves resolution down to 18 nm (dense features).¹⁶ In order to improve the resolution beyond 22 nm, the off-axis-illumination mode quadruple shaped annular¹⁷ was used on the NXE 3300B for the discussed work.

III. RESULTS AND DISCUSSION

The goal of this study was to demonstrate high resolution patterning of a spin on glass photoresist (HSQ) using a commercial EUV scanner. Typically, resist thickness scales with the patterns to be printed (smaller patterns/features need thinner resist to obtain the desired feature size). Conventional resists [e.g., chemically amplified resist (CAR)] have a low etch resistance and relatively low thickness, necessitating the use of a pattern transfer layer (i.e., a hardmask/underlayer) for effective pattern transfer into the underlying substrate. Moreover, the effect of standing waves can be reduced with the use of antireflecting coatings. Hence, typical EUV exposures use resist underlayers for reducing the effect of standing waves and also for maintaining the fidelity of the

pattern transfer. Depending on the resist and application, the patterning stack can vary. In this study, HSQ resist was first exposed using standard Si-anti-reflection coating (Si-ARC) and organic dielectric layer (ODL). The Si-ARC should reduce unwanted reflections within the resist stack and ODL serves as a dielectric patterns transfer layer.

A. Initial EUV exposure experiments using HSQ resist

In our initial experiment, we exposed HSQ resist that was spin coated onto layers of Si-ARC and ODL. The deposited thicknesses of Si-ARC and ODL were 18 and 60 nm, respectively. An increasing dose array of 2 to 88 mJ/cm^2 was used with fixed nominal wafer focus of $-0.075\ \mu\text{m}$ for the trilayer stack. A post-exposure bake (PEB) was performed at 80°C for 60 s. Last, the sample was developed for 30 s in 0.26 N TMAH developer.

The extremely poor contrast which resulted made it impossible to perform in-line CD SEM measurements. As a result, in order to determine the degree of resist exposure, optical microscopy was performed on the wafer. The

Fig. 2. (a) EUV patterned stack of resist with underlayers on the substrate. For example, underlayer-1 could be an ARC and underlayer-2 could be an ODL. (b) A simplified patterning stack consisting of only HSQ resist spin coated on the Si-substrate.

(a) Line to space (L/S) ratio 1:2

10 nm

12 nm

14 nm

16 nm

18 nm

(b) Line to space (L/S) ratio 1:3

10 nm

12 nm

14 nm

16 nm

18 nm

FIG. 3. CD-SEM images of HSQ patterns on a Si substrate, without any underlayer, ranging from 10 to 18 nm (the far left column 10 nm and the far right column being 18 nm). (a) Target L/S of 1:2 showing 14 nm and lower CD patterns with partial cut and bridging. (b) Target L/S of 1:3 showing 12 and 10 nm with partial cut.

TABLE I. CD and LWR measurements on 1:2 and 1:3 L/S pattern types with CDs ranging from 10 to 18 nm. The LWR is higher and this database provides a baseline in ironing out the required parameters for future tweaking.

Target pattern	Measured CD (nm)	Measured LWR (nm)	Dose (mJ/cm ²)
10 nm 1:2 (L/S)	10.0	7.8	63
12 nm 1:2 (L/S)	13.1	7.4	67
14 nm 1:2 (L/S)	12.2	7.6	52
16 nm 1:2 (L/S)	14.0	9.2	59
18 nm 1:2 (L/S)	13.3	8.2	59
10 nm 1:3 (L/S)	10.1	7.7	67
12 nm 1:3 (L/S)	9.1	6.5	68
14 nm 1:3 (L/S)	13.1	8.9	63
16 nm 1:3 (L/S)	15.6	7.7	63
18 nm 1:3 (L/S)	17.0	9.6	63

appearance of the field suggested that macrolevel pattern transfer occurred, but that increased dose was needed to fully resolve patterns on wafer. Furthermore, the thickness of the resist underlayers may need to be adjusted for optimization. This result suggests that during HSQ exposure in EUV, the photoelectrons generated by the Si-substrate might be playing an important role in HSQ crosslinking mechanism. As a result, when these low energy electrons penetrate through the underlayers, they lose their energy, causing the lower yield in the available electrons for the HSQ exposure. Thus, we determined that it would be a significant process modification in order to print the desired patterns.

As an alternative to the standard multilayer resist stack, a simplified single-layer HSQ resist stack was also tested. Since, HSQ resist post-exposure converts the resist to a primarily silicon oxide based material, the direct pattern transfer to the Si-substrate is feasible. Notably, pattern transfer from HSQ resist to a Si-substrate using a HBr plasma etch has been

FIG. 4. Cross-section SEM images of 14, 16 and 18 nm 1:3 L/S patterns showing (a) tilted SEM images, and (b) orthogonal SEM showing the tapered nature of the profile for 60 s development.

(a) Line to space (L/S) ratio 1:2

(b) Line to space (L/S) ratio 1:3

FIG. 5. In-line CD-SEM images of HSQ patterns on Si substrates without any underlayer, ranging from 10 to 18 nm. (a) Target L/S of 1:2 showing improvement in profile with no bridging between high resolution patterns, and (b) Target L/S of 1:3 showing continuous patterns.

reported in literature.¹⁸ This approach would eliminate the need for the underlayers/hard mask for pattern transfer. As a result, the simplified patterning stack consisting of spin coating of HSQ resist on the Si-substrate was tested. Figure 2 depicts the patterned stack. It also shows the patterned stack with underlayers.

In order to determine the dose baseline for the stack without underlayers, a dose array of 2–88 mJ/cm² was applied. The nominal wafer focus was maintained at $-0.075 \mu\text{m}$. For chemically amplified resist (CAR), the use of a PEB step is important, in order to complete the reaction initiated during the exposure.¹⁹ Since HSQ is a non-CAR, there is no specific need for the PEB step, except to potentially reduce the effect of standing waves in the film. For process simplification, the PEB step was removed. As mentioned before, for standard, in-line fab processing, low concentration developer is more typical (0.26N TMAH). To avoid underdevelopment, the developer time was increased to 60 s in this experiment. The CD-SEM images of the resulting patterns (from 10 to 18 nm with the L/S of 1:2 and 1:3) are shown in Fig. 3. Table I provides information on dose and measured line width roughness (LWR) for the initial single-layer HSQ exposure. The results of this initial study demonstrated that single-layer HSQ resist could be patterned using EUV exposure; however, the LWR was very high. Furthermore, the patterns of 14 nm CDs and lower (except 14 nm 1:3 L/S) were partially cut and/or had bridging issues.

Following in-line CD-SEM analysis, individual die were cross-sectioned and subjected to SEM for the 14, 16, and 18 nm 1:3 (L/S). These patterns were chosen because they were fully resolved without any bridging or fouling.

As observed in Fig. 4, the shape of the resist profile is tapered. This may have been caused by a shift in focus, due to the altered stack height (as compared to the multilayer resist stack). Thus, a follow-up study was performed, with the objective of improving patterning resolution and profile shape, while also reducing LWR.

B. Exposures with varying focus and a narrow dose range

In our initial experiments, the EUV exposure dose range was varied from 2 to 88 mJ/cm² for determining the dose baseline. From Table I, it was observed that the average dose was $\sim 63 \text{ mJ/cm}^2$ for the fixed focus. Thus, in our follow-on study, the dose range was narrowed to a range of 58–68 mJ/cm². Narrowing the dose range enabled us to subsequently explore the optimum focus-dose condition for the line/space patterns on our reticle. For these experiments, wafer focus was varied from $-0.075 \pm n 0.030 \mu\text{m}$ (where $n = 0, 1, 2, 3$). Last, the development time was further increased to 120 s in order to reduce bridging between printed lines. Figure 5 shows the results of this study.

Initial observations from CD-SEM micrographs show that removal of the underlayer and adjustment of the focus/exposure conditions resulted in improved pattern resolution. As compared to results from the previous conditions, 14 nm and smaller patterns resolved as continuous lines, without

TABLE II. CD and LWR measurements on 1:2 and 1:3 L/S pattern types with CDs ranging from 10 to 18 nm. The data show improvement in the LWR with revised conditions.

Target pattern	Measured CD (nm)	Measured LWR (nm)	Dose (mJ/cm ²)	Focus (μm)
10 nm 1:2 (L/S)	10.0	6.5	62	0.015
12 nm 1:2 (L/S)	12.4	7.8	65	-0.045
14 nm 1:2 (L/S)	13.9	5.9	66	0.015
16 nm 1:2 (L/S)	16.0	6.2	65	-0.015
18 nm 1:2 (L/S)	18.0	6.2	66	-0.015
10 nm 1:3 (L/S)	10.0	5.5	64	0.015
12 nm 1:3 (L/S)	9.9	5.7	67	-0.045
14 nm 1:3 (L/S)	13.9	6.0	66	-0.015
16 nm 1:3 (L/S)	15.6	5.7	66	-0.015
18 nm 1:3 (L/S)	17.4	5.2	66	-0.015

FIG. 6. Cross-sections of 14, and 18 nm 1:3 L/S from (a) tilted SEM, and (b) orthogonal SEM for the optimized 120 s development/varying focus process.

bridging. Table II provides information on the dose, LWR, and focus for the above analysis.

The results in Table II show that LWR was reduced, except for 10 and 12 nm 1:2 (L/S), which had no significant LWR improvement. The LWR for the 18 nm 1:3 (L/S) was improved the most. Cross-sectional SEM of patterned lines was performed to study the resist profile. Figure 6 shows SEM of cross-sections for 14 nm 1:3 and 18 nm 1:3 lines.

The cross-section SEM images in Fig. 6 show that the resist profile shape was improved (versus the previous exposure conditions), suggesting that longer development time with focus corrections improve sidewall shape. However, the taper observed in the resist profile might be attributed to the role of photoelectrons generated from the Si-substrate, which

could play a lead role in HSQ crosslinking, making optimization of process parameters difficult. Thus, a follow-up study is required to understand the extent of contribution of electrons generated from the substrate and their role in HSQ exposure.

On the other end, these conditions result in continuous patterns and no bridging. Some patterns had a spacing offset, which could potentially be due to function of the exposure tool (EUV scanner) or unknown mask bias.

C. Effects of longer development time

In the Fig. 7(a), CD-SEM data from 10 to 18 nm dense patterns with similar process conditions (as mentioned in

FIG. 7. CD-SEM images of HSQ patterns on Si substrate without any underlayer ranging from 10 to 18 nm. The target L/S was 1:1 and resist development time was varied between (a) 120 s development time and (b) 160 s development time.

FIG. 8. Plot showing comparison of (a) CD and (b) LWR for both 120 and 160 s development times for a range of 1:2 and 1:3 L/S patterns.

Sec. III B) for 120 s development time are presented. As shown in this figure, the 18 nm pattern was the only one that resolved. Moreover, the 18 nm dense patterns appeared under-developed and showed bridging. The development time was further increased with the objective of resolving dense patterns.

The HSQ devolvement rates gradually decrease and eventually stop with time.^{20,21} In order to resolve dense patterns, we increased the development time from 120 to 160 s. Figure 7(b) shows the result of this increase for dense patterns (1:1 L/S). Moreover, the effect on increased development time on the semidense features is shown in Fig. 8.

The images shown in Fig. 7(b) suggest that 160 s of development time for 0.26 N TMAH developer did not result in any improvement for resolving dense patterns. For resolving dense patterns, the proximity effect of the electrons also needs to be considered, as they can cause the unwanted resist exposure creating the resist scum,²¹ which would adversely affect resolution of dense patterns. One of the ways to reduce the contribution from the proximity effect is to use the lower dose for resolving the dense patterns. The plot in Fig. 8 compares the CD and LWR for 120 and 160 s of development time, respectively.

As observed in Fig. 8, there was little improvement in LWR. For the semidense patterns, the longer development time decreased the line-width for the target CD. As a future direction, longer development times should be explored for 0.26 N TMAH developer on EUV patterned HSQ.

IV. CONCLUSIONS AND FUTURE DIRECTIONS

We successfully developed a process flow for high resolution HSQ patterning using a commercial HVM scanner. The developed process without any underlayers not only provides flexibility in reducing process steps at deposition but also the pattern transfer can directly be done on the substrate. The inline developed process can be used to test and develop various process based on high resolution HSQ patterns. The study on increased development time suggested that while sub-dense patterns went further reduced in line-width, there was no change in resolving the dense patterns. As a future direction; the effect of lower dose (to reduce proximity effect), “dipole” off axis illumination mode and the longer development time can be studied as the potential means to resolve dense patterns. Moreover, further studies can be conducted for understating EUV exposure mechanism in HSQ and the potential role of photoelectrons generated from the

Si-substrate in HSQ cross-linking. This may also help in understanding the factors limiting the resolution.

ACKNOWLEDGMENTS

The authors acknowledge SUNY Polytechnic Institute Colleges of Nanoscale Science and Engineering for providing the support for this work. Furthermore, the authors would like to thank Susan Wiand from CNSE for her help with Hitachi-5200 SEM. The authors would also like to thank Yu Jen Fan for assisting with resist outguessing test using EUVT. They thank Brain Martinick for the helpful discussion.

- ¹A. E. Grigorescu, M. C. van der Krogt, and C. W. Hagen, *Proc. SPIE* **6519**, 65194A (2007).
- ²I. Junarsa, M. P. Stoykovich, P. F. Nealey, Y. Ma, F. Cerrina, and H. H. Solak, *J. Vac. Sci. Technol., B* **23**, 138 (2005).
- ³A. G. Caster, S. Kowarik, A. M. Schwartzberg, O. Nicolet, S. H. Lim, and S. R. Leone, *J. Raman Spectrosc.* **40**, 770 (2009).
- ⁴S. Cabrini and S. Hawata, *Nanofabrication Handbook* (CRC, Boca Raton, FL, 2012), p. 38.
- ⁵H. Namatsu, Y. Takahashi, K. Yamazaki, T. Yamaguchi, M. Nagase, and K. Kurihara, *J. Vac. Sci. Technol., B* **16**, 69 (1998).
- ⁶D. L. Olynick, B. Cord, A. Schipotinin, D. F. Ogletree, and P. J. Schuck, *J. Vac. Sci. Technol., B* **28**, 581 (2010).
- ⁷R. A. Lawson and A. P. G. Robinson, "Overview of materials and process for lithography," in *Materials and Process for Next Generation Lithography* (Elsevier, Amsterdam, Netherlands, 2016), p. 13.
- ⁸Y. Ekinici, M. Vockenhuber, B. Terhalle, M. Hojeij, L. Wang, and T. R. Younkin, *Proc. SPIE* **8322**, 83220W (2012).
- ⁹Y. Ekinici, M. Vockenhuber, M. Hojeij, L. Wang, and N. Mojarad, *Proc. SPIE* **8679**, 867910 (2013).
- ¹⁰N. Mojarad, J. Gobrecht, and Y. Ekinici, *Sci. Rep.* **5**, 9235 (2015).
- ¹¹N. Mojarad, M. Hojeij, L. Wang, J. Gobrecht, and Y. Ekinici, *Nanoscale* **7**, 4031 (2015).
- ¹²P. W. Wachulak, M. G. Capeluto, M. C. Marconi, D. Patel, C. S. Menoni, and J. J. Rocca, *J. Vac. Sci. Technol., B* **25**, 2094 (2007).
- ¹³Y. Ekinici, "Extreme UV interference lithography: progress and prospects," in *SPIE Newsroom* (2013).
- ¹⁴Y. Ekinici, H. H. Solak, C. Padeste, J. Gobrecht, M. P. Stoykovich, and P. F. Nealey, *Microelectron. Eng.* **84**, 700 (2007).
- ¹⁵J. K. W. Yang and K. K. Berggren, *J. Vac. Sci. Technol., B* **25**, 2025 (2007).
- ¹⁶ASML, "TWINSCAN NXE:3300B," https://www.asml.com/products/systems/twincan-nxe/twincan-nxe3300b/en/s46772?dfp_product_id=842.
- ¹⁷J. Finders, J. V. Schoot, M. Mulder, A. Hunter, M. Dusa, B. Socha, and P. Jenkins, "DUV lithography (KrF) for 130 nm using off-axis illumination and assisting features," in *SEMICON Japan* (1999).
- ¹⁸D. Morecroft, J. K. W. Yang, S. Schuster, K. K. Berggren, Q. Xia, W. Wu, and R. S. Williams, *J. Vac. Sci. Technol., B* **27**, 2837 (2009).
- ¹⁹C. Mack, *Fundamental Principles of Optical Lithography: The Science of Microfabrication* (Wiley, West Sussex, England, 2007), pp. 23–24.
- ²⁰J. K. W. Yang, B. Cord, H. Duan, K. K. Berggren, J. Klingfus, S.-W. Nam, K.-B. Kim, and M. J. Rooks, *J. Vac. Sci. Technol., B* **27**, 2622 (2009).
- ²¹H.-S. Lee, J.-S. Wi, S.-W. Nam, H.-M. Kim, and K.-B. Kim, *J. Vac. Sci. Technol., B* **27**, 188 (2009).