EUV lithography using Multi-Trigger Resist at low dose and high resolution

C. Popescu[1], G. O'Callaghan[1], C. Storey[1], A. McClelland[1], J. Roth[2], E. Jackson[2], A.P.G. Robinson[1*]

(1) Irresistible Materials, Birmingham Research Park, Birmingham, UK
(2) Nano-C, 33 Southwest Park, Westwood, MA, USA.
**a.p.g.robinson@bham.ac.uk*

Novel resist materials will be required to support high-NA EUV. Resolution, roughness and dose requirements are compounded by a decreased depth of focus, which will affect both the resist and the underlayer and stack if pattern transfer is to be maintained. Furthermore, as pitches and film thickness are reduced, metrology is becoming increasingly difficult. Irresistible Materials (IM) is developing novel resists based on the multi-trigger concept. In a multi-trigger resist (MTR) multiple elements must be simultaneously activated to enable a catalytic reaction. Chemical contrast and resolution are enhanced due to a dose dependent intrinsic quenching behaviour. MTR shows good lithographic results and wide flexibility. MTR Gen1 introduced tuneable absorbance as high as 18µm^{-1}. MTR Gen2.1 and 2.2 increased monomer activation rate and optimised the ring opening polymerisation reactions, allowing p28 line/space and p34 hexagonal pillars to be patterned across a wide dose range (20–60, and 30–80mJ/cm^2, respectively). Gen2.4 and Gen2.5 combined the separate approaches for further improvements and NXE data shows 40% sensitivity increase of Gen2.4 over Gen2.1 with no LWR change. Here we present the continuing evolution of the MTR system, discussing UL impact on p34 and p32 hexagonal pillar defectivity, LCDU and sensitivity.

Keywords: EUV lithography, photoresist, non-CAR, molecular resist, multi-trigger resist, chemical amplification

1. Introduction

Intensive research for suitable resist materials to support the next generation EUV lithography, including the implementation of high-NA lithography, continues. It is commonly thought that development of new photoresist mechanisms is required as existing chemically amplified resists (CAR) will be unable to pattern the tightest pitches, and thus non-chemically amplified resists (non-CAR) are drawing more attention than ever before. Specifically, resists used for the current technology nodes are expected to reach a plateau in performance when it comes to simultaneously achieving the ultimate resolution, low line edge roughness, high sensitivity and low defectivity required in high-NA. [1–3] However, there remain many unknowns, which are slowing the resist development and implementation, the most important being the mechanism by which the EUV photons interact within the photoresist film.

The energy of EUV photons is well above the ionization threshold of the resist materials, and thus photochemical approaches are not necessarily optimal in the EUV regime. The shift to secondary electron chemistry permits novel approaches to be developed. However, the mechanism of low energy electron interaction with resist molecules are not yet entirely clear and research to reveal the resist mechanism is ongoing. [4] Several approaches to explain photoacid generation have been proposed. These have included the ionization of the general resist matrix leading to electron recombination with photoacid generators producing photoacids either directly [5] or indirectly [6]. More recent work led by Brainard and co-workers, however, suggests an alternative mechanism based on internal excitations contributing to acid generation.. [4,7]

Underlayer choice can also play a very important role in the overall performance of resists. The events occurring at the interface between the photoresist and the silicon wafer are modulated by the chemical composition and the physical properties of the underlayer. This can be helpful or deleterious to the resolution and roughness in the features patterned, for instance by modulating the resist adhesion. The generation of secondary electrons in the underlayer may also be important. [8,9]. Thermal properties of the underlayer may impact the speed of the resist chemistry. Furthermore, the underlayer choice also affects the metrology introducing contrast variations, depending on the underlayer used, in non-intuitive ways. [10] Finally, as industry moves towards the implementation of high-NA EUV to enable further improvements in resolution, it will become increasingly important to consider the overall thickness of the resist/ underlayer stack. It has long been known that the achievable post development film thickness has needed to reduce, as pitch sizes decrease, to avoid pattern collapse, [11] and that this trend is accelerating [12]. However, film thicknesses will be further suppressed in high-NA, as the depth of focus of the tool is known to be severely constrained. [13] The metrology issues will also be exacerbated, and optimisation of the underlayer/ photoresist stack will need to increase, whilst ever thinner photoresists will also introduce pattern transfer challenges. [14]

Irresistible Materials have developed the multi trigger resist (MTR) resist platform to address the on-going requirements of EUV lithography. The MTR material is a molecular resist, which utilises ring-opening polymerisation (ROP) and incorporates a unique self-quenching mechanism, known as the multi-trigger mechanism, directly in the chemical pathways, to improve performance. The intrinsic self-quenching mechanism in the MTR material, which has been described before [15–21] provides an advantage in acid diffusion mitigation and offers a benefit on achieving ultimate resolutions with low edge roughness. After the development of the initial prototype of the resist, MTR Generation 1 (Gen1) was developed, incorporating non-metal organic high-opacity moieties for high photo-absorption. Transfer of lines and pillar patterns from MTR films using SiN as a hard mask and standard etch processes, even from thin films (26 nm post-coat; 24 nm post-development) has been demonstrated. [22]

MTR Generation 2 (Gen2) was introduced in 2022, and initial results were presented [23]. In particular, good lithographic performance was shown for P28 L/S with doses below 20 mJ/cm^2 and p36 and p34 hexagonal pillars with doses below 30 mJ/cm^2. [22, 23] More recently we have explored three separate routes to significantly improve the Z-factor of the MTR system, either by increasing the activation rate of the monomer activation (Gen2.1); adjusting the relative reaction rates of the initiation and propagation rates of the ROP (Gen2.2); and via a more efficient multi-trigger quenching mechanism (Gen2.3). Additionally, the advantages gained by each

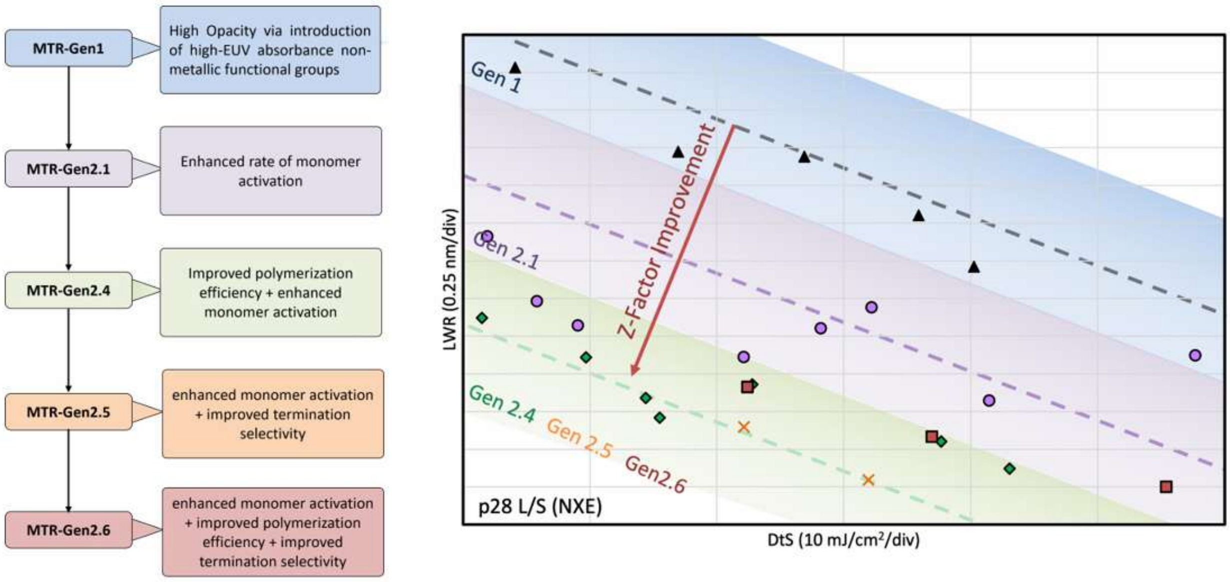


Figure 1: Schematic depicting the MTR evolution (left), together with indicative patterning performance (right). (Triangle - MTR Gen1; Circle - MTR Gen2.1; Diamond - MTR Gen 2.4, Cross – MTR Gen 2.5, Square - MTR Gen2.6). All data collected at p28 on the NXE3400.

present new data showing the improvement shown by Gen 2.4, and also Gen 2.6, where all three improvement routes are combined (see figure 1).

2. Experimental

The resist samples were prepared by dissolving the individual components in ethyl lactate. The solutions were then combined in various weight ratios and concentrations to give a range of formulations. The solutions undergo metal ion removal using 3M Zeta Plus filtration disks to reduce metals to levels appropriate for fab-based processing.

The resist was spun onto a commercial organic underlayer, Brewer Scientific Optistack® AL412 for line / space patterning, and an alternative organic underlayer, "Underlayer-2 (UL-2)", for pillar patterning, unless stated. After spin-coating of the resist the samples received a post application bake (PAB) of 80°C for 1 minute, using a track for film deposition, and the samples were exposed to EUV using an ASML NXE3400 scanner at imec. After exposure the samples received a post exposure bake of 65°C unless stated and were developed in Fujifilm DP819A developer for 30 seconds using a dynamic system with no subsequent rinse. The patterning was observed using a Hitachi CD-SEM (model 5000, 6300 or GT2000) and the LWR, LER, and LCDU values are biased values as measured inline unless otherwise stated. For select wafers, MetroLER analysis using an appropriate number of images (25 for pillars, 50–100 for p28 lines) at each dose was carried out to calculate unbiased LWR, LER and LCDU numbers, and also calculate the defectivity (e.g. merged or missing pillars) for the sample.

3. Results

3.1 Optimisation of MTR Gen2.4 for p28 dense lines and spaces

By varying the relative ratios of the MTR Gen 2.4 components it is possible to provide a resist with

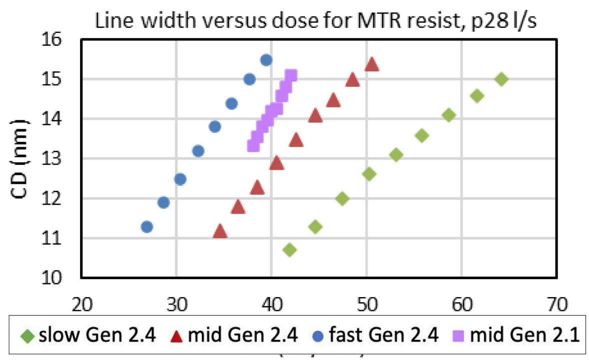


Figure 2: P28 L/s patterning in MTR Gen 2.1 and Gen2.4, line width versus dose. Exposed using the NXE3400 and analysed using MetroLER.

higher or lower sensitivity, depending on the application requirements. An experiment for dense line/spaces was carried out changing the formulation ratio to provide three different sensitivity resists. In addition to this, a Gen 2.1 resist with a dose midway between the Gen 2.4 'fast' and Gen 2.4 'mid' resist was patterned and compared. The spun film thickness for L/S was 20–22nm and no PEB was applied. The wafers all underwent MetroLER analysis and the unbiased LER and defectivity have been plotted. As seen in

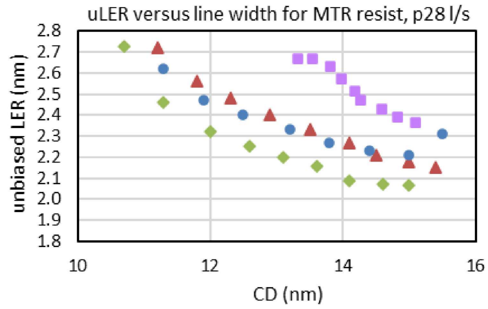
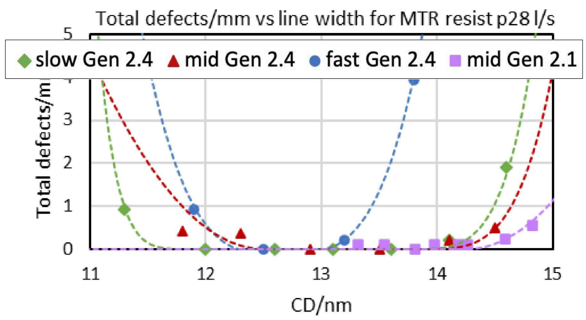


Figure 3: P28 L/s patterning in MTR Gen 2.1 and Gen2.4, unbiased LER versus line width..

figure 2, the dose to achieve 14nm lines can be varied from 34 mJ/cm² to 58mJ/cm².



Examining figure 3 which shows unbiased LER versus line width, shows that the slow Gen 2.4 has significantly lower LER than the other samples, albeit at a higher dose and all generations of Gen 2.4 resist have lower roughness than the Gen 2.1 resist. The results also suggest that the 'fast' Gen 2.4 resist gives similar roughness values to a resist ('mid' Gen 2.4) that requires 9mJ/cm² more dose. However less sensitive formulations show a wider failure free window for defects, as shown in figure 4. MetroLER analysis suggests that the failure free window for the 'slow' Gen 2.4 resist is at least from 12.0 nm to 13.6 nm (0 defects/mm) with <5 defects/mm between 11.3 nm and 14.6 nm linewidth (3.3 nm total window).

3.2 Results for p32 hexagonal pillars on organic UL-2

Evaluation of MTR Gen2.4 resist for p32 hex pillars was conducted by patterning the resist on a 5 nm thick bespoke organic underlayer (UL-2) at a spun film thickness of 21 nm. Gen 2.4 'Fast' can pattern p32 hexagonal pillars with a diameter of 15.8 nm at a dose of 42 mJ/cm², whilst Gen 2.4 'Slow' takes a dose of 72 mJ/cm² to pattern the same diameter (unbiased figures). The crucial question regards the impact of this dose difference on both the LCDU and defectivity of the pattern. The defectivity of these pillars will manifest as missing pillars in the underdosed region and touching pillars in the overdosed region. The unbiased LCDU values are very similar up to around 17nm pillar diameter, and are only 0.1nm

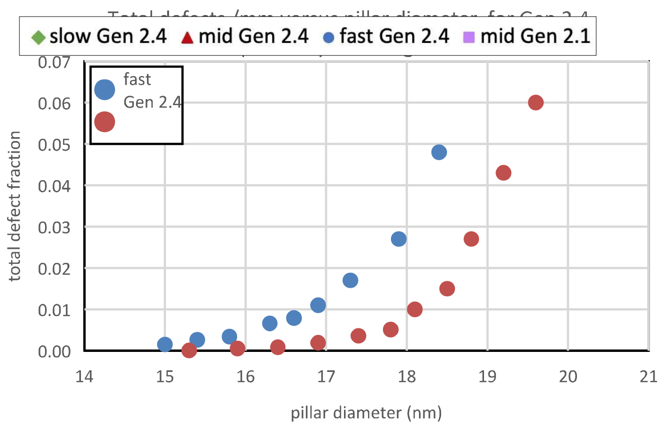
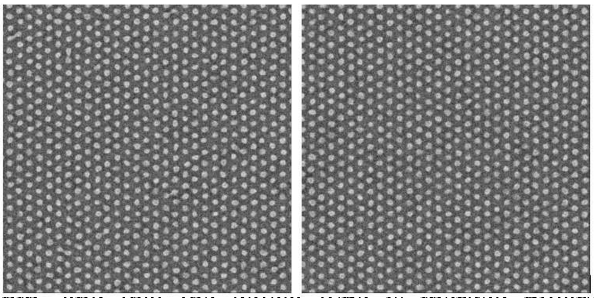


Figure 5: Pillar diameter versus total defect fraction (measured via MetroLER) for 2 different Gen 2.4 resists. All exposures undertaken on the NXE3400, and with otherwise identical patterning and processing conditions.

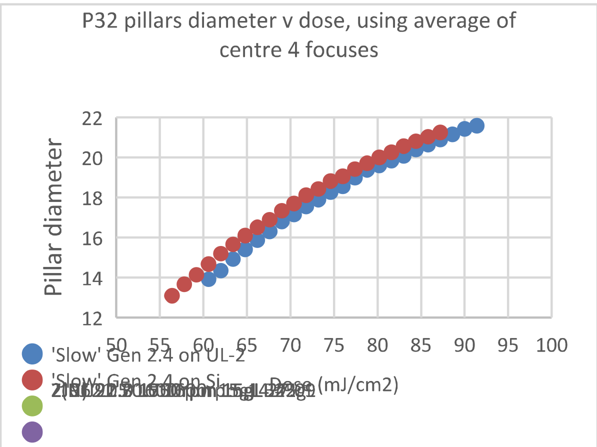
different at 18 nm pillar diameter. The minimum LCDU is 2.3 nm for the 'slow' resist and 2.4 nm for the 'fast' resist. This metric by itself may



nm, and that the defect type is merged pillars

Figure. 6: pillars patterned on the NXE3400 at p32 hex: (left) MTR Gen2.4 'fast', dose 43.1 mJ/cm²; diameter 16.3 nm, unbiased LCDU 2.79 nm; (right) MTR Gen2.4 'slow', dose 74.1 mJ/cm²; diameter 16.4 nm, unbiased LCDU 2.71 nm.

MTR resist has occurred using organic underlayers, with some preferred underlayers such as UL-2 having material properties which enable patterning with lower roughness and defectivity. However, as shown previously [22], MTR resist can be patterned directly onto SiN and used to transfer patterns. In figure 7, we show MTR Gen 2.4 resist patterned directly on Silicon and compared to patterning on organic UL-2. In this



case, we see a 3mJ/cm² reduction in dose to size when patterning on silicon (top), and a 0.2nm reduction in LCDU when patterned on silicon (bottom). The patterning on silicon also results in fewer defects when patterning in the14nm to 17nm diameter pillar region.

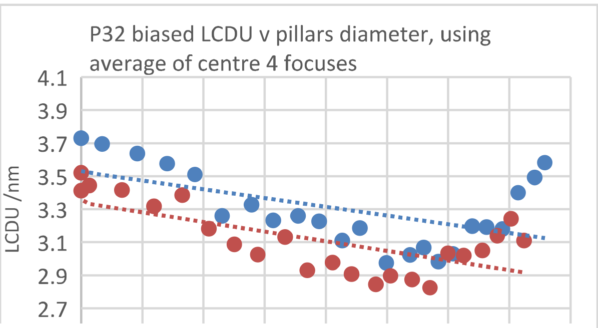


Fig. 7 Pillar diameter versus dose, and biased LCDU versus diameter for p32 hex pillar patterning on NXE3400 on UL-2 and Si

touching pillars when using a thicker film shows itself in the higher LCDU figure. Figure 9 shows the staggered pillars at 18nm diameter.

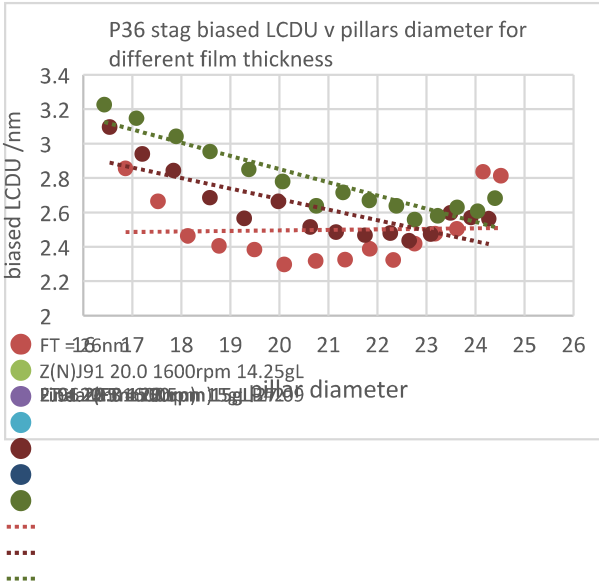


Fig. 8: Biased LCDU versus diameter for p36 staggered pillar patterning on NXE3400 on Si for a 'fast' Gen 2.4 resist

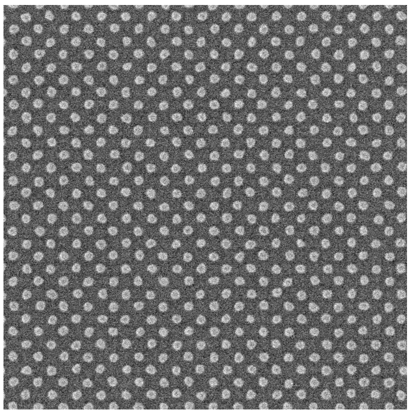


Fig. 9: p36 staggered pillars patterned on NXE3400 using a fast MTR Gen2.4 resist, dose 39mJ/cm2, diameter 18.2nm, biased LCDU 2.5nm

4. Conclusion

MTR Resist is a negative tone resist with an intrinsic dose dependent quenching mechanism, which can pattern high resolution patterns with EUV lithography. The lithographic performance of several MTR formulations was shown. By modifying the MTM molecule, crosslinker and PAG, both individually and in combination, we can optimize the reaction rates in the MTR mechanism. Different combinations have been designated Gen 2.1 to Gen 2.6 and here we show an LWR improvement in Gen 2.4 combinations. We presented the lithographic performance at pitch 28 nm dense line/space where 14.1 nm wide lines were patterned at 59 mJ/cm^2 with an unbiased LER of 2.09 nm using a Gen 2.4 resist. We showed hexagonal pillar results: pitch 32 nm patterned at 43 mJ/cm^2 to obtain a pillar diameter of 16 nm with an unbiased LCDU of 2.8 nm and additionally, p32 pillars of 16 nm diameter were patterned at 74 mJ/cm^2 with an unbiased LCDU of 2.7 nm. We also showed data that showed that staggered pillars at p36 can be patterned at 40mJ/cm^2 for a biased pillar diameter of 18nm.

Performance improvements such as reduced roughness and defectivity can also be shown to be affected by choices such as underlayer and developer. We showed that using silicon, or in the future silicon based layers, under the resist is a feasible alternative to an organic underlayer for pillars.

Acknowledgements

The authors thank Irresistible Materials Ltd. and Nano-C for support and provision of resist materials. The authors would like to thank Chris Mack and Bill Usry from Fractilia for providing MetroLER measurements, and to Roberto Fallica from imec also for MetroLER measurements.

References

[1] Nagahara, S., Que Dinh, C., Yoshida, K., Shiraishi, G., Kondo, Y., Yoshihara, K., Nafus, K., Petersen, J.S., De Simone, D., Foubert, P., Vandenberghe, G., Stock, H-J, Meliorisz, B., “EUV resist chemical gradient enhancement by UV flood exposure for improvement in EUV resist resolution, process control, roughness, sensitivity, and stochastic defectivity,” *Proc. SPIE*, **11326** (2020) 113260A.

[2] Shirotori, A., Hoshino, M., De Simone, D., Vandenberghe, G., Matsumoto, H., “A novel main chain scission type photoresists for EUV lithography”, *Proc SPIE*, **11517** (2020) 115170D.

[3] Sharma, S.K., Kumar, R., Chauhan, M., Moinuddin, M.G., Peter, J., Ghosh, S., Pradeep, C.P., Gonsalves, K.E., “All-new nickel-based Metal Core Organic Cluster (MCOC) resist for N7+ node patterning,” *Proc SPIE*, **11326** (2020) 1132604.

[4] Torok, J., Del Re, R., Herbol, H., Das, S., Bocharova, I., Paolucci, A., Ocola, L. E., Ventrice Jr., C., Lifshin E., Denbeaux, G., Brainard, R. L., “Secondary Electrons in EUV Lithography,” *J Photopolym. Sci. Technol.*, **26** (2013) 625–634.

[5] Thackeray, J., Cameron, J., Jain, V., LaBeaume, P., Coley S., Ongayi O., Wagner M., Rachford A., Biafore J., “Progress in Resolution, Sensitivity and Critical Dimensional Uniformity of EUV Chemically amplified Resists,” *Proc. SPIE*, **8682** (2013) 868213.

[6] Nakano, A., Kozawa, T., Okamoto, K., Tagawa, S., Kai, T., Shimokawa, T., “Acid Generation Mechanism of Poly(4-hydroxystyrene)-Based Chemically Amplified Resists for Post-Optical Lithography: Acid Yield and Deprotonation Behavior of Poly(4-hydroxystyrene) and Poly(4-methoxystyrene),” *Jpn. J. App. Phys.* **45**, (2006) 6866–6871.

[7] Narasimhan, A., Wisehart, L., Grzeskowiak, S., Ocola, L.E., Denbeaux, G., Brainard, R. L., “What we don’t know about EUV exposure mechanisms," J Photopolym. Sci. Technol., **30** (2017) 113–120.

[8] Long, L.T., Neureuther, A., Walraff, G., Naulleau, P. "Resist Underlayer Simulations," In *IEUVI TWG April 2022*, 7, (2022), http://ieuvi.org/TWG/Resist/IEUVI_Resist01.htm (Accessed 13/02/2023).

[9] Raley, A., Huli, L., Grzeskowiak, S., Lutker-Lee, K., Krawicz, A., Feurprier, Y., Liu, E., Kato, K., Nafus, K., Dauendorffer, A., Bae, N., LaRose, J., Metz, A., Hetzer, D., Honda, M., Nishizuka, T., Ko, A., Okada, S., Ido, Y., Onitsuka, T., Kawakami, S., Fujimoto, S., Shimura, S., Dinh, C.Q., Muramatsu, M., Biolsi, P., Mochiki, H. and Nagahara, S., "Outlook for high-NA EUV patterning: a holistic patterning approach to address upcoming challenges," *Proc SPIE*, **12056** (2022) 120560A.

[10] Severi, J., Lorusso, G.F., De Simone, D., Moussa, A., Saib, M., Duflou, R., De Gendta, S., “Chemically amplified resist CDSEM metrology exploration for high NA EUV lithography,” *J Micro/Nanopattern. Mater. Metrol.*, **21** (2022) 021207.

[11] Goldfarb, D.L., Bruce, R.L., Bucchignano, J.J., Klaus, D.P., Guillorn, M.A. and Wu, C.J., "Pattern collapse mitigation strategies for EUV lithography," *Proc SPIE,* **8322** (2012) 832205.

[12] Noga, D.E., Lawson, R.A., Lee, C.T., Tolbert, L.M. and Henderson, C.L., "Understanding pattern

collapse in high-resolution lithography: impact of feature width on critical stress." *Proc* SPIE, **7273** (2009) 727334.

[13] Burov, A., Pret, A.V. and Gronheid, R., "Depth of focus in high-NA EUV lithography: a simulation study." *Proc SPIE,* **12293** (2022) 122930V.

[14] Fallica, R., De Simone, D., Chen, S., Safdar, M. and Suh, H.S., "Scaling and readiness of underlayers for high-NA EUV lithography," *Proc* SPIE, **12292** (2022) 122920V.

[15] Vesters, Y., McClelland, A., Popescu, C., Dawson, G., Roth, J., Theis, W., de Simone, D., Vandenberghe, G., Robinson, A.P.G, "Multi-trigger resist patterning with ASML NXE3300 EUV scanner," *Proc. SPIE*, **10586** (2018) 1058308.

[16] Popescu, C., Kazazis, D., McClelland, A., Dawson, G., Roth, J., Theis, W., Ekinci, Y., Robinson, A.P.G., "High-resolution EUV lithography using a multi-trigger resist," *Proc SPIE*, **10583** (2018) 105831L.

[17] O'Callaghan, G., Popescu, C., McClelland, A., Kazazis, D., Roth, J., Theis, W., Ekinici, Y., Robinson, A.P. G., "Multi-trigger resist – Novel synthesis improvements for high resolution EUV lithography," *Proc SPIE*, **10960** (2019) 109600C.

[18] Montgomery, W., McClelland A., Ure D., Roth J., Robinson A., "Irresistible Materials multi-trigger resist: the journey towards high volume readiness," *Proc SPIE*, **10143** (2017) 1014328.

[19] Popescu, C., McClelland, A., Kazazis, D., Dawson, G., Roth, R., Ekinci, Y., Theis, W. and Robinson, A. P.G., "Multi-trigger resist for electron beam and extreme ultraviolet lithography," *Proc SPIE*, **10775** (2018) 1077502.

[20] Popescu C., O'Callaghan G., McClelland A., Roth J., Lada T., Robinson A.P.G., "Performance enhancements with high opacity multi-trigger resist," *Proc SPIE*, **11326** (2020) 1132611.

[21] Popescu, C., O'Callaghan, G., McClelland, A., Roth, J., Lada, T., Kudo, T., Dammel, R., Moinpour, M., Cao, Y., Robinson, A. P. G., "Progress in the multi-trigger resist," *Proc SPIE*, **11612** (2021) 116120K.

[22] Popescu, C., O'Callaghan, G., McClelland, A., Roth, J., Jackson, E., Robinson, A. P. G., "Component optimization in the multi-trigger resist," *Proc SPIE*, **12055** (2022) 120550G.

[23] Popescu, C., O'Callaghan, G., McClelland, A., Storey, C., Roth, J., Jackson, E. and Robinson, A.P.G., " Recent accomplishments in EUV lithography patterning for multi-trigger resist," *Proc SPIE*, **12292** (2022) 122920E.

[24] Popescu, C., O'Callaghan, G., McClelland, A., Storey, C., Roth, J., Jackson, E. and Robinson, A.P.G., "EUV lithography patterning using multi-trigger resist," *Proc SPIE*, **12498** (2023) 1249812.

[25] Lawson, R.A., Frommhold, A., Yang, D.X., Robinson, A.P.G, "Negative-tone organic molecular resists," In *Frontiers of Nanoscience: Materials and Processes for Next Generation Lithography*, **Vol. 11**, Robinson A.P.G. and Lawson R.A. eds., (Oxford: Elsevier, 2016). pp. 223-317.