Investigating High Opacity and Increased Activation Energy in the Multi-Trigger Resist

C. Popescu\textsuperscript{a}, G. O’Callaghan\textsuperscript{a}, A. McClelland\textsuperscript{a}, J. Roth\textsuperscript{b}, T. Lada\textsuperscript{b}, T. Kudo\textsuperscript{c}, R. Dammel\textsuperscript{d}, M. Moinpour\textsuperscript{e}, Y. Cao\textsuperscript{c}, and A.P.G. Robinson\textsuperscript{a}

\textsuperscript{a}Irresistible Materials, Birmingham Research Park, Birmingham, UK
\textsuperscript{b}Nano-C, 33 Southwest Park, Westwood, MA, USA.
\textsuperscript{c}EMD Performance Materials Corp, 70 Meister Ave., Somerville, NJ 08876, USA
\textsuperscript{a}p.g.robinson@bham.ac.uk

The development of novel EUV resists is widely agreed to be one of the highest priority challenges for the deployment of high-NA EUV lithography. One potential approach is the multi-trigger concept wherein a reaction will only occur when multiple elements of the resist are initiated concurrently and in close spatial proximity. The multi-trigger material presented consists of a novel MTR molecule and a crosslinker, which represent the resist matrix, together with a photoacid generator (PAG). Research is continuing to upgrade this resist, in particular focusing on improving resist opacity and crosslinking density. Here we present results from further work focused on the enhancement of the high-opacity MTR resist. A new high-Z crosslinker molecule, mark III, has been synthesized and formulated in the MTR resist to make the high opacity MTR compatible with the ethyl lactate and PGMEA casting solvents. We report results obtained using the new MTR system containing this high-Z crosslinker mark III, with a variation of process conditions and formulation variations. The lithographic performance of a formulation containing this crosslinker, at pitch 32nm patterned on an NXE3350 is presented. Furthermore, we have also investigated increasing the activation energy of the self-quenching aspect of the MTR system. In the case presented, MTR8 has a higher activation energy than MTR4. Having a higher activation energy is predicted to allow the introduction of PEB to increase crosslinking and reduce pattern collapse, whilst simultaneously preserving the self-quenching behaviour. We present results which show a decrease in dose and Z-factor using MTR8 at this formulation ratio compared to MTR4.

Keywords: EUV lithography, Photoresist, Molecular resist, Multi-trigger resist, Chemical amplification, Crosslinking

1. Introduction

As EUV lithography becomes established in high volume manufacturing it has been necessary to address many challenges with the tool and the materials. EUV photoresists that have the appropriate capability to support future roadmap requirements remain a challenging topic. Currently traditional chemically amplified resists (CAR) are being used, but several novel approaches are being investigated to support future patterning needs for high resolution and sensitivity and low line width roughness and stochastic defects. [1–3]. It is, however, well-known that these resist metrics are fundamentally linked in a tradeoff relationship, and improvements to one often comes at a cost to another. For instance, the resolution of a CAR can be improved by reducing the addition diffusion length with base additives or bulky acids, but with a detrimental effect on the required dose and/or the line width roughness. Defectivity due to line collapse, bridging or line breaks is an increasingly common failure mode at pitches below 32nm.

Irresistible Materials (IM) is developing novel resist systems based on the multi-trigger concept. In a multi-trigger resist multiple elements of the resist must be simultaneously activated to enable the catalytic reactions to proceed. In high dose areas the resist therefore behaves like a traditional CAR, whilst in low dose areas, such as line edges, the reaction is second-order increasing the chemical...
Effectively there is a dose dependent quenching-like behavior built into the resist, enhancing chemical contrast and thus resolution and reducing roughness, whilst eliminating the materials stochastics impact of a separate quencher.

In a chemical amplified resist (CAR) (see Figure 1, left hand diagram) the photoacid (H+) reacts with a resist molecule and is immediately regenerated. The resist molecule is altered from unexposed to exposed in a single step. Quenchers and catalytic inefficiencies remove H+, or reactions stop at the end of the PEB, but otherwise the reaction will continue indefinitely. In a multi-trigger material, resist exposure proceeds via a catalytic process in a similar manner to a chemically amplified resist. However, instead of a single photoacid causing a single resist exposure event and then being regenerated, in the multi-trigger resist multiple photoacids activate multiple acid sensitive molecules, which then react with each other to cause a single resist event while also regulating the photoacids (Figure 1, right hand diagram). In areas with a high number of activated photoacids (higher dose areas, for instance at the centre of a pattern feature) resist components are activated in close proximity and the multistep resist exposure reaction proceeds, ending with photoacids regeneration and thus further reactions, ensuring high sensitivity. In areas with a low number of activated photoacids (lower dose areas, for instance at the edge of a pattern feature), the activated resist components are too widely separated to react, the photoacids are not released and are thus removed, stopping the catalytic chain. The multi-trigger resist creates an increase in the chemical gradient at the edge of patterned features, and reduces undesirable acid diffusion out of the patterned area.

The multi trigger effect is due to the synergistic combination of two main reaction pathways together with a number of lesser pathways. We can control the weighting of these pathways through formulation choices. In effect there are six different aspects of the resist formulation that can be varied to affect the performance, see figure 2. In the MTR platform previously presented [4-10] it is possible to vary the relative importance (or ratio) of each aspect with a relatively high degree of flexibility, to achieve various performance changes. Whilst performance can be modulated through the formulation ratios, further enhancements are possible by optimizing the functional groups.

Research has been undertaken to improve this resist, in particular focusing on improving resist opacity and crosslinking density. Higher absorption is a potential route to overcome the photon shot noise limit in EUV lithography as well as potentially improving the sensitivity to enable high volume manufacturing at current source power output. IM have added a high Z non-metal element onto the crosslinker component of the resist. The formulations that has been tested often also does not include an additional quencher which further reduces the chemical stochastics, whereas a extrinsic quencher was necessary with the standard
crosslinker to minimize LWR. The results presented here show the third iterations of this high opacity crosslinker. A mark III high-Z crosslinker was synthesized with a modified chemical structure in order to improve the solubility in industry recommended solvents.

2. Experimental

The resist samples were prepared by dissolving the individual components in ethyl lactate or PGMEA. The solutions were then combined in various weight ratios and concentrations to give a range of formulations.

The resist was spun onto a commercial underlayer, Brewer Scientific E2 STACK AL412-302. After spin-coating of the resist the samples received a post application bake (PAB) of 80 °C for 1 minute, when using a track for film deposition, or 60 °C for 3 minutes at PSI. EUV exposures were performed using the XIL-II interference lithography tool at the Paul Scherrer Institute, Switzerland [7], and using an ASML NXE3350 scanner. After exposure most samples did not receive a post exposure bake but were developed in n-butyl acetate for 60 seconds followed by 15 seconds of MIBC rinse unless stated. Some of the samples received a post exposure bake of up to 80 °C for 1 minute where noted in the results section. For the NXE3350 results, the patterning was observed using CD-SEM and the LWR and LER values are biased values unless otherwise stated, and where the all LER and LWR numbers are unbiased, 3\sigma, they are measured using Fractilia software. At PSI, exposed samples were analyzed with a scanning electron microscope (SEM) in top-down view. Critical dimension (CD), LWR and LER were calculated from the SEM images with SMILE software. The baseline for the optimization is the previously introduced xMT resist system, shown in Figure 3, from which the MTR1 series resist was developed. The molecular resin has been modified, to increase the glass transition temperature (Tg) (MTR2) and to modify the activation energy of the molecule (MTR4 and MTR8). A cross-linking molecule, which incorporates a non-metal high-Z element, was introduced in the system for increased optical density. Triphenylsulfonium tosylate, which acts as a photo-decomposable quencher in epoxy-based systems, was added. [8].

3. Results and discussion

3.1. High Z crosslinker (mark III)

The Mark I high-Z Crosslinker chemical structure previously presented [11] was once more modified to enable solubility in industry accepted solvents Ethyl (-L) lactate and PGMEA, and the lithographic performance at pitch 32 nm patterned on an NXE3350 containing this crosslinker is presented in Figures 4 and 5.

The film thickness is 22.5 nm and no PEB was used. A biased LWR of 4.2 nm for a line width of 15.1 nm was shown. Using Fractilia software, an unbiased LWR value of 3.82nm was calculated at best dose / best focus and the dose-to-size is
There are some bridging defects still seen at higher doses, so further improvements to the formulation, including ways increase the purity of the formulation are being undertaken. Trackside process variations to evaluate their effects on bridging, include underlayer choice, and developer and rinse conditions are underway. One process variation which was explored was introducing a post exposure bake (PEB). A PEB of 60 °C resulted in a reduction in dose to 46mJ/cm² however the LWR increased by 0.2nm at pitch 32nm. A further increase in PEB temperature to 80 °C resulted in a further dose to size decrease to 41mJ/cm² and a further 0.3nm LWR increase. Overall, the lowest Z factor conditions occur with a PEB of 60°C and is 4.1 x 10⁻⁸ using biased LWR values.

### Table: Process Variations

| Dose (mJ/cm²) | Rectangular Scan | CD (nm) | LWR (nm) |
|----------------|-------------------|---------|----------|
| 42             | ![Image]          | 12.41   | 4.70     |
| 45             | ![Image]          | 13.28   | 4.65     |
| 48             | ![Image]          | 14.15   | 4.60     |
| 51             | ![Image]          | 15.07   | 4.22     |
| 54             | ![Image]          | 15.58   | 4.48     |
| 57             | ![Image]          | 16.68   | 4.18     |

Fig. 4. MTR4L3Y(2)-0 negative tone resist patterned at pitch 32 nm.

3.2 Process variation – film thickness for MTR4L3Y(2)

The thickest film thickness tested using the NXE3350 was 22.5 nm. A film thickness of 20nm negatively affected LWR, so increasing the film thickness could be favourable at p32 using the NXE scanner. At PSI, 12 nm lines on a 28 nm pitch were patterned with an LWR of 2.07 nm using a film thickness of 25 nm. This used a 60 °C PEB and the analytics were carried out by SMILE software. Also patterned at PSI were 13 nm lines on a 26 nm pitch using an 18 nm film thickness. These results are shown in figure 6.

3.3 Comparing MTR molecules with different activation energies

MTR4 and MTR8 molecules were synthesised...
54 mJ/cm². There are some bridging defects still seen at higher doses, so further improvements to the formulation, including ways to increase the purity of the formulation, are being undertaken. Trackside process variations to evaluate their effects on bridging, including underlayer choice, and developer and rinse conditions, are underway. One process variation that was explored was introducing a post-exposure bake (PEB). A PEB of 60 °C resulted in a reduction in dose to 46 mJ/cm²; however, the LWR increased by 0.2 nm at pitch 32 nm. A further increase in PEB temperature to 80 °C resulted in a further dose to size decrease to 41 mJ/cm² and a further 0.3 nm LWR increase. Overall, the lowest Z factor conditions occur with a PEB of 60 °C and is 4.1 x 10⁻⁸ using biased LWR values.

3.2 Process variation – film thickness for MTR4L3Y(2)

The thickest film thickness tested using the NXE3350 was 22.5 nm. A film thickness of 20 nm negatively affected LWR, so increasing the film thickness could be favourable at p32 using the NXE scanner. At PSI, 12 nm lines on a 28 nm pitch were patterned with an LWR of 2.07 nm using a film thickness of 25 nm. This used a 60 °C PEB and the analytics were carried out by SMILE software. Also patterned at PSI were 13 nm lines on a 26 nm pitch using an 18 nm film thickness. These results are shown in figure 6.

3.3 Comparing MTR molecules with different activation energies

MTR4 and MTR8 molecules were synthesised. For MTR4L3Y(2)-0: Left: Focus versus critical dimension; Right: Focus versus LWR. In this case, MTR8 has a higher activation energy than MTR4. In the MTR2 resist, it is seen that a PEB is beneficial to mitigating pattern collapse, but detrimental to LWR. Having a higher activation energy should allow introduction of a PEB to increase crosslinking and reduce pattern collapse whilst avoiding an increase in LWR. The results shown in figure 7 show a decrease in dose and Z-factor using MTR8 at this formulation ratio compared to MTR4, when tested at PSI. The results also show a Z factor improvement when using a 60 °C PEB, and initial results indicate that higher activation energies do not show the significant rise in LWR with PEB that was previously observed in lower activation energy formulations.

4. Conclusion

It has been shown previously that Multi-Trigger chemistry enhances the chemical gradient without quenchers. Previous formulations have shown little benefit from PEB. The high-Z MTR chemistry, however, can be driven using external factors such as PEB. New synthesis procedures have been developed to produce novel molecules capable of improving the Irresistible Materials Multi Trigger resist, which had previously shown 16 nm patterning on an NXE3300 scanner. Improved absorption, reduced material stochastics and improved crosslinking are being addressed, and the materials’ patterning capabilities have been shown at PSI, at the MET and on an NXE3350 scanner using EUV lithography.

In this study, a new high-Z crosslinker molecule, mark III, has been synthesized and introduced in the MTR resist to make the high opacity MTR compatible with ethyl lactate and PGMEA casting solvents. We report results obtained using the new MTR system containing the high-Z cross-linker mark III, with a variation of process conditions and
formulation variations. The lithographic performance at pitch 32 nm patterned on an NXE3350 containing this crosslinker is presented. A biased LWR of 4.2 nm for a line width of 15.1 nm is shown. Introducing a PEB induces performance changes for the MTR4L3Y(2) resist. The sensitivity improves by over 20% with 80 °C PEB. However, the LWR does increase with PEB by 12%. Overall, the lowest Z factor (using biased LWR) occurs with a 60 °C PEB temperature. The Z factor is also significantly lower with FT 22.5 nm compared to 20 nm. The thickest film tested using the NXE3350 is 22.5 nm. However, at PSI, 12 nm lines on a 28 nm pitch were patterned with an LWR of 2.07 nm using a film thickness of 25nm.

We have also increased the activation energy of the MTR system. In this case, MTR8 has a higher activation energy than MTR4. Having a higher activation energy should allow introduction of PEB to increase crosslinking and reduce pattern collapse. We present results which show a decrease in dose and Z-factor using MTR8 at this formulation ratio compared to MTR4, when tested at PSI. The results also show a Z factor improvement when using a 60 °C PEB.

Acknowledgements

The authors would like to thank Ms Michaela Vockenhuber, Dimitrios Kazazis, Tim Allenet and Chia-Kai Yeh from PSI for their assistance with the EUV exposures. Part of this work was performed at Swiss Light Source (SLS), Paul Scherrer Institute, 5232 Villigen, Switzerland. The authors would like to thank Marie Krysak (Intel) and Warren Holcomb and Chanin King (Lawrence Berkeley National Laboratory) for their help with EUV exposures. The authors would like to thank Lidia van Lent-Protasova, Jara Santa Garcia (ASML) for their help with EUV exposures. The authors would like to thank the Engineering and Physical Sciences Research Council (EPSRC) for support of this project. The authors thank Irresistible Materials Ltd. and Nano-C for support and provision of resist materials. This project has received funding from the EU-H2020 research and innovation program under grant agreement No 654360 having benefitted from the access provided by Paul Scherrer Institute in Villigen, Switzerland within the framework of the NFFA-Europe Transnational Access Activity.

References

[1] S. Nagahara, C. Que Dinh, K. Yoshida, G. Shiraishi, Y. Kondo, K. Yoshihara, K. Nafus, J. S. Petersen, D. De Simone, P. Foubert, G. Vandenberghe, H-J. Stock, and B. Meliorisz, *Proc. SPIE*, **11326** (2020) 113260A.
[2] A. Shirotori, M. Hoshino, D. De Simone, G. Vandenberghe, and H. Matsumoto, *Proc. SPIE*, **11517** (2020) 115170D.
[3] S. K. Sharma, R. Kumar, M. Chauhan, M. G. Moinuddin, J. Peter, S. Ghosh, C. P. Pradeep, and K. E. Gonsalves, *Proc. SPIE*, **11326** (2020) 1132604.
[4] Y. Vesters, A. McClelland, C. Popescu, G. Dawson, J. Roth, W. Theis, D. de Simone, G. Vandenberghe, and A. P. G. Robinson, *Proc. SPIE* **10586** (2018).
[5] C. Popescu, D. Kazazis, A. McClelland, G. Dawson, J. Roth, W. Theis, Y. Ekinci, and A. P. G. Robinson, *Proc. SPIE*, **10583** (2018) 10583.
[6] G. O’Callaghan, C. Popescu, A. McClelland, D. Kazazis, J. Roth, W. Theis, Y. Ekinci, and A. Robinson, *Proc. SPIE* **10960** (2019).
[7] W. Montgomery, A. McClelland, D. Ure, J. Roth, and A. Robinson, *Proc. SPIE*, **10143** (2017) 1014328.
[8] C. Popescu, A. McClelland, D. Kazazis, G. Dawson, R. Roth, Y. Ekinci, W. Theis, and A. P. G. Robinson, *Proc. SPIE*, **10775** (2018) 10775-02.
[9] Y. Ekinci, M. Vockenhuber, B. Terhalle, M. Hojeij, L. Wang, and T. R. Younkin, *Proc. SPIE*, **8322** (2012) 83220W.
[10] R. A. Lawson, A. Frommhold, D. X. Yang, and A. P. G. Robinson, “Negative-tone organic molecular resists,” in Robinson A.P.G., Lawson R.A. editors. Materials and Processes for Next Generation Lithography. Oxford, Elsevier (2016).
[11] C. Popescu, G. O’Callaghan, A. McClelland, J. Roth, T. Lada, and A. P. G. Robinson, *Proc. SPIE*, **11326** (2020) 11326-11.