Multi Trigger Resist for EUV Lithography

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Irresistible Materials (IM) is developing novel resist systems based on the multi-trigger concept, which incorporates a dose dependent quenching-like behaviour. The multi trigger resist (MTR) is a negative tone crosslinking resist that does not need a post exposure bake (PEB). In this study, we present the results that have been obtained using MTR resists by performing EUV exposures on the ASML NXE3300B EUV scanner at IMEC, and also at PSI and the MET tool at Berkeley. We present the lithography performance of the MTR2 resist series, which has been designed for lower line edge roughness. The MTR2 resist shows 16nm half pitch lines patterned with a dose of 38mJ/cm2, giving a LER of 3.7 nm on the NXE3300. Performance across various process conditions is discussed. We also present a new resist formulation using a crosslinker with a high opacity non-metallic atom attached, which has patterned 13nm lines at PSI and MET.

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

1. Introduction

Recent tool and source advances make the introduction of EUV lithography into high volume manufacturing in the very near future highly probable. Whilst traditional chemically amplified resists will likely support the initial insertion, a wide range of materials options are being examined for future nodes [1–3], aiming to identify a photoresist that simultaneously meets the resolution, line edge roughness and sensitivity requirement. However, this issue represents a fundamental trade-off in lithography (the RLS triangle) and it is difficult to overcome. For instance, addition of quenchers in chemically amplified resists reduces the acid diffusion length and increases the resolution of the patterned features, but decreases the sensitivity, and impacts on material stochastics affecting the line edge roughness.

The newly introduced Irresistible Materials (IM) multi-trigger resist concept [4,5] has been designed to address the trade-off relationship between sensitivity, resolution and LER. The multi-trigger concept employed in our system enables high sensitivity but also incorporates a dose dependent quenching behaviour into the chemistry to improve resolution and reduce the materials stochastics impact of a separate quencher. The multi-trigger material consists of an MTR molecule and a crosslinker, which together represent the resist matrix, together with a photoaacid generator (PAG). EUV light generates photoacids, as with a traditional chemically-amplified resist (CAR), but the response of the resist matrix implements a logic-type function. Photoacids will activate matrix molecules but the reaction will only proceed where an MTR molecule and a crosslinker are simultaneously activated in close proximity to each other. In this case the matrix molecules will react
together and release both acids. Where a matrix molecule is activated without an active counterpart in proximity then the acid will be retained without an exposure reaction occurring, thus removing the acid from the reaction. This behaviour allows a high sensitivity response at a certain dose threshold, but turns the resist response off much more quickly as the dose decreases, which should lead to sharper lines and lower LER.

MTR resist can provide a single resist solution to hybrid patterning approaches incorporating i-line, 193 nm, EUV and electron beam patterning. [6-8], but in this study we present the results of our EUV development of MTR resists, screened at the PSI tool and the Berkeley MET. We also present results of exposures using an ASML NXE3300 scanner using this resist system. We show results obtained by driving the resist behaviour towards the MTR regime, and through formulation variations, and present our strategy of work to improve the lithographic performance of our resist system.

2. Experimental
The resist samples were prepared by dissolving the individual components in ethyl lactate, and then purifying the samples using a metal ion reduction system. Resists were formulated with different weight ratios of these individual components, to drive the resist behaviour in different directions. For the NXE patterning, the resists were coated using a TEL Lithius ProZ track. The resist was spun onto a commercial underlayer, Brewer Scientific E2 STACK AL412-302.

After the spin-coating of the resist the samples received a post application bake (PAB) of 60°C for 180 seconds. EUV exposures were performed using the XIL-II interference lithography tool at the Paul Scherrer Institute, Switzerland [9,10] and using the MET at the Lawrence Berkeley National Laboratory, USA. Exposures were also realized on ASML NXE3300 at IMEC using different custom illumination settings for line-and-spaces pattern (dipole-like). After exposure the samples did not receive a post exposure bake but were developed in n-butyl acetate followed by a methyl isobutyl carbinol (MIBC) rinse.

At IMEC, the patterning was observed using CD-SEM Hitachi CG-5000, with 500eV and 8pA as beam conditions, and 16 frame images were taken with a magnification of 150k x 150k for square images (2048 x 2048 px) or 150k x 49k for rectangular scan (1024 x 1024 px). CD, LWR and LER values are reported either biased or unbiased. The biased values are measured using the CD-SEM software on rectangular scan images. To obtain unbiased roughness values, 50 square images of the pattern were taken at different position on one die and were then analyzed using metroLER™ software from Fractilia to remove SEM noise from the PSD graphs (as per imec protocol cfr [11]).

The baseline for the optimization is the previously introduced xMT resist system, shown in Fig. 1, from which the MTR1 series resist was developed.

The molecular resin has more recently been modified, to increase the glass transition temperature ($T_g$) (MTR2).

Triphenylsulfonium tosylate, which acts as a photo-decomposable quencher in epoxy based systems, was added where indicated [12].

3. Results
The MTR2 formulation uses an enhanced variant of the molecular resin designed to increase $T_g$, compared to the baseline MTR1200 formulation, and this was assessed using EUV
lithography at PSI using 14nm HP dense lines. Figure 2 (bottom) shows that the performance of MTR2200 is improved over the MTR1200 formulation, with the sensitivity being maintained whilst the LER improved from 4.3 nm to 3.1 nm.

3.1. Varying the MTR component ratio

In order to investigate the extent to which one is able to control the MTR behaviour we have varied the concentration of the MTR component in various formulations and observed the effect. A higher MTR ratio enables a higher multi trigger effect. Table 1 shows that dose increases linearly with increasing MTR ratio, and that the LER improves with increased loading, with the optimum level in the 0.4 region. These results were with formulations without quencher and patterned at PSI.

| MTR222x Ratio | LER (nm) | Dose (mJ/cm²) |
|---------------|---------|---------------|
| 0.2           | 6.5     | 23.3          |
| 0.4           | 4.8     | 36.6          |
| 0.6           | 5.1     | 53.0          |
| 0.8           | 6.1     | 66.5          |

Samples MTR2200 (with standard MTR ratio) and MTR2204 (with increased MTR ratio) were patterned using the NXE3300 at IMEC. Both formulations included a quencher at the same level. These formulation changes should reduce and control the diffusion of acid in the resist. In Fig. 3, we can see that it permits both samples to resolve 16nm HP patterning.

Similarly, the enhanced multi-trigger behaviour of MTR2204 sample helps for a better chemical edge definition, translated into improved roughness. The unbiased LER of MTR2204 at 16nm HP is 3.7 nm, versus 4.9 nm for the MTR2200. In parallel to this roughness improvement, the quenching mechanism induced by multi-trigger impacts here also significantly the sensitivity, with roughly a doubling of the dose to size.

3.2. Thickness impact

In order to optimize the patterning conditions and mitigate the different failure modes in
patterning such as wiggling of lines, we patterned MTR2200 at various thicknesses from 18.5 nm to 22.5 nm and exposed at PSI, as seen in Fig. 4. It can be seen that a difference of 0.5 nm in the film thickness will impact both the dose required to pattern a given CD but also the LER. From the results obtained in the variable thickness experiments it can be concluded that the optimum film thickness required to pattern 16 nm dense lines with our resist is 22.5 nm or higher and 18.5 nm for 14 nm dense lines. This is mainly due to pattern collapse for the thicker films for the smaller features. This leads us to conclude that the effect is due to the aspect ratio of the resist.

We then studied this effect in more detail using patterning on the NXE3300. For MTR2200 and MTR2204, we have coated the resist at different film thickness varying from 22 to 34 nm, and then exposed to EUV. Overall for larger half pitches, LWR and LER roughness is decreased with thicker resist film. The 20nm HP pattern at high film thickness of both resist is pictured in Fig. 5, showing performances on a par with low dose CAR resist [13] at same pitch.

Nevertheless, if we look at the PSD spectra of the LER, as reported in Fig. 6, we can see that both low frequency roughness and the correlation length is increased with an increasing thickness. As the LWR PSD(0) keeps decreasing while the LER PSD(0) is increasing with increasing film thickness, it is an indication that the photoresist suffers wiggling at higher film thickness.

Furthermore, the impact of film thickness on resolution is drastic: for 27nm FT and above, both resist show strong pattern collapse and are not able to resolve 16nm HP pattern anymore. This pattern collapse is more pronounced for MTR2204 due to its higher sensitivity. As shown in Fig. 6, the LER PSD(0) is increasing with increasing film thickness, indicating wiggling of the pattern.

Fig. 4. The effect of resist film thickness on the dose and LER.

Fig. 5. (Left) MTR2204 at 34nm film thickness (after coating), patterned at 20nm HP, at a dose of 44.5 mJ/cm². Unbiased roughness values of LWR 2.9 nm and LER 2.6 nm were measured. (Right) MTR2200 at 33nm FT after coating, 20nm HP, dose 28 mJ/cm², unbiased LWR and LER are 3.2 nm and 2.8 nm, respectively.

Fig. 6. Power spectral density curves of 20nm HP pattern of MTR2200 at various film coating thicknesses. Even though general roughness decreases, the low frequency roughness is increasing, indicating wiggling.
collapse at low aspect ratio (above 1.5) partially comes from poor adhesion with the underlayer. Another root cause could be an insufficient stiffness of the material. Further development of the chemistry, notably targeting at achieving higher crosslinking density in the material, might help to improve the pattern collapse margin, and is a current focus of investigation for Irresistible Materials.

3.3. Using alternative crosslinker with high Z atom

IM have synthesised a crosslinker that contains the high opacity non-metallic atom, CL3, and a new formulation, MTR2620 was created and tested at the MET in Berkeley. The patterning performance is presented in Fig. 7 and shows 13.3 nm and 17.5 nm semi-dense lines with low LER values, particularly for the 17.5nm lines. The dose required to pattern these features is higher than desired, therefore further synthesis and formulation work looked at increasing sensitivity.

An alternative formulation ratio MTR262Z(2) designed to improve sensitivity, was patterned at

![Fig. 7. Top-down SEM images of MTR2620 (Top) pitch 40 nm, CD 13.3 nm, LER 4.24 nm; (Bottom) 86.8 mJ/cm², pitch 48 nm, CD 17.5 nm, LER 2.80 nm.](image)

PSI, as shown in Fig. 8. This shows 12.7nm lines patterned at a pitch of 28 nm with a dose of 53 mJ/cm² with an LER of 4.2 nm. The sensitivity of the resist formulation has thus improved, and sub 13nm lines at a dense pitch are possible.

4. Conclusion

We have shown that there are a number of materials and formulation routes to improve LER in our resist system; using the MTR2 formulation rather than MTR1 reduced the LER by 1.2 nm at pitch28nm at PSI, and varying the film thickness has a pronounced effect on dose, LER and particularly pattern collapse at hp14nm at PSI. Varying the MTR component ratio in the system showed that the best LERs are achieved at 0.4 and 0.6 MTR ratios for MTR22x. Multi-trigger resist patterning capabilities were tested using NXE3300B scanner and 16nm HP dense line-space patterns were resolved. The MTR2204 formulation showed a roughness of only 3.7nm LER (unbiased) for a dose of 38.5 mJ/cm² at 16nm HP. Increasing the thickness of the film permits roughness reduction but induced wiggling and pattern collapse. We have introduced also a crosslinker into the resist system with a high-Z non-metallic crosslinker, which patterns 13nm lines at BMET. Increasing the sensitivity of the resist using this crosslinker, and increasing the crosslinking within the film to decrease pattern collapse will be future areas of research.

Acknowledgements

The authors would like to thank Ms Michaela Vockenhuber 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 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. The Disco DAD 321 waffer dicer used in this research was obtained through the Birmingham Science City provided: Creating and Characterizing Next Generation Advanced Materials, with support from Advantage West Midlands (AWM) and part funded by the European Regional Development Fund (ERDF). C. P. thanks The University of Birmingham for support. 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.

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