

# Process and Sensitivity Optimisation of the Multi-Trigger Resist

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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. In this study, we present the results that have been obtained using Multi Trigger Resists (MTR) by performing EUV exposures on the ASML NXE3300B EUV scanner at IMEC, where the MTR is a negative tone crosslinking resist incorporating high opacity atoms. Pitch 28nm dense patterns can be patterned at a dose of 59mJ/cm<sup>2</sup>, a line width of 12.5nm, and a biased LWR of 3.91nm. These resist formulations have also been used to pattern 20nm diameter pillars on a hexagonal 40nm pitch with a dose of 51mJ/cm<sup>2</sup>, and a CDU of 3.5nm; and also pillars at pitches of 34nm hexagonal with a dose of 80mJ/cm<sup>2</sup> to achieve 17.5nm diameter pillars. High photospeed approaches, which have patterned p28 lines and p34 hex pillars at sub-30 mJ/cm<sup>2</sup> doses are also introduced.

**Keywords:** EUV lithography, photoresist, molecular resist, multi-trigger resist, chemical amplification, crosslinking

## 1. Introduction

EUV lithography is starting to be established in high volume manufacturing but there are still many challenges with the tool and the materials. EUV photoresists with the appropriate capability to support future roadmap requirements such as high NA remain a high priority area of research. Currently traditional chemically amplified resists (CAR) [1] 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. [2–4]. It is however, well-known that these resist metrics are fundamentally linked in a tradeoff relationship, and improvements to one often comes to the detriment of another. As an example, the resolution of a CAR can be improved by reducing the addition diffusion length with base additives or bulky acids, but with an unfavourable 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 32 nm.

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 gradient. Effectively there is a dose dependent quenching-like behaviour built into the resist, enhancing chemical contrast and thus resolution and reducing roughness, whilst eliminating the materials stochastic impact of a separate quencher.

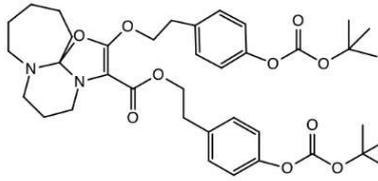
MTR utilises a catalytic ring opening propagation mechanism (CROP). The reaction front is a percolation, controlled by varying the relative reaction rates of initiation and propagation mechanisms. The incorporation of a proprietary dose dependant control molecule accelerates the reaction in high dose areas; in mid dose areas it quenches the photoacid and blocks (but does not quench) propagation; and in low dose areas it quenches all resist reactions. As the control molecule participates in the crosslinking mechanism it will not be leached out during development. The MTR mechanism also leads to film densification, which enhances etch durability.

In the MTR platform previously presented [5-11] 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. The baseline for the optimization is the previous system.

Figure 1 shows the previous system.

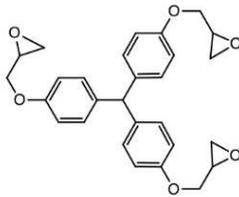
**Molecular Resin (xMT)**



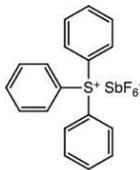
line xMT

introduce which molecular glass transition modify the (MTR4 and XL-A, with elements in the system. Triphenyls photo-de systems, can be further the function

**Crosslinker (CL1)**



**Photo-acid generator (PAG1)**



1)from oped. The increase the 2) and to molecule molecule, al high-Z iced in the density. acts as a n epoxy-based 1st performance mulation ratios, by optimizing

Research has been undertaken to improve this negative tone 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. EUV lithography suffers from the low volume of photons produced [13]. To address this, we have synthesised crosslinkers that have elements that have high EUV absorbance compared to carbon, hydrogen and oxygen [14]. The elements chosen have high EUV absorbances, are relatively straightforward to incorporate into a resist and are *non-metal*.

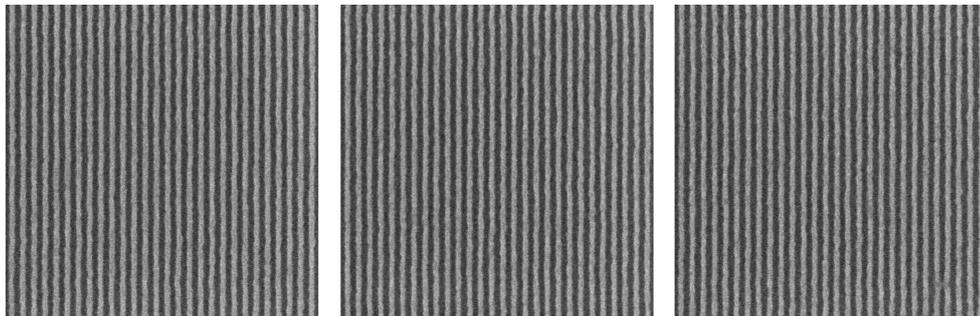
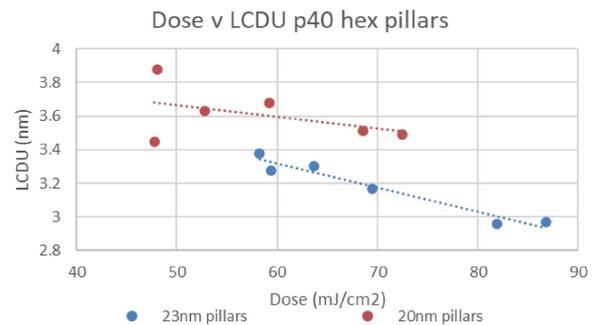


Figure 2: MTR resist with XL-A: Left: PEB 60 °C, Dose 58.75 mJ/cm<sup>2</sup>, CD: 12.49 nm, LWR: 3.91 nm; Middle PEB 65 °C, Dose 56.5mJ/cm<sup>2</sup>, CD 12.00nm, LWR 4.17nm; Right: PEB 70°C, Dose 55.75 mJ/cm<sup>2</sup>, CD: 12.01 nm, LWR: 4.37 nm.

## 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 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.. After spin-coating of the resist using a track for film deposition, the samples received a post application bake (PAB) of 80 °C for 1 minute, and exposed using an ASML NXE3400 scanner at imec. After exposure the samples received a post exposure bake of between 60°C and 70°C, and were developed in n-butyl acetate for 30 seconds using a dynamic system with no subsequent rinse. The patterning was observed using Hitachi CD-SEM (CG-5000 or 6300 models) with 500eV and 8pA as beam conditions, and the LWR, LER, LCDU and CER values are biased values unless otherwise stated.



## 3. Results

Trials at pitch 28nm line space were carried out on formulations using XL-A and MTR 2, to assess the resolution of this crosslinker as a baseline. A narrow sweep of PEB temperatures from 60 °C to 70 °C was used to find the optimum temperature for

minimum Z factor for XL-A at a film thickness of 20.5nm (figure 2). A negatively biased mask was used with a line width on the reticle designed at 12nm. It was found that for XL-A the optimum PEB temperature was between 60°C and 65°C, with both temperatures having a Z factor of  $1.01 \times 10^{-8}$  (where Z factor = (Resolution)<sup>3</sup> × (LWR)<sup>2</sup> × (Sensitivity)) for 12nm width lines. At 60 °C the dose required to pattern 12nm lines was 57.6mJ/cm<sup>2</sup>, and at 65 °C it was 56.7mJ/cm<sup>2</sup>. The average biased LWR was 4.20nm for 60°C and 4.23nm for 65°C.

### 3.2 Tunability of MTR resist

One of the most striking aspects of MTR resist is the feature to tweak the resist formulation slightly by changing the ratio of the solid components (indicated in figure 1) and impacting the lithography outcome quite significantly, with the sensitivity of the resist being a readily apparent change. One aspect that was explored was to change the amount of quenching in the system and to investigate the impact on the and LCDU and CER of pillar patterning. A systematic experiment was designed where the amount of MTR molecule (MTR8) and the amount of photo-decomposable quencher, was varied within a narrow set of values. The results from 6 different formulations (all using the crosslinker XL-A) carried out using pillars arranged in an hexagonal pattern at pitch 40nm. The reticle used is designed with 23nm diameter pillars. As can be seen in table 1, a 33% reduction in dose to size can be achieved by using resist 3 rather than the baseline resist (resist 1). The increase in LCDU is 14%. By using, for example, resist 5, a 20% dose reduction can be achieved with less than a 7% increase in LCDU.

The graph in figure 3 shows that for all the resist formulations there is a general linear trend of

Resist	Dose to size (mJ/cm <sup>2</sup> )	Percentage reduction in dose	LCDU/nm	Percentage increase in LCDU
baseline	86.76		2.97	
3	58.21	-32.9	3.38	13.8
2	59.42	-31.5	3.27	10.2
4	63.66	-26.6	3.30	11.1
5	69.46	-19.9	3.17	6.7
6	81.91	-5.6	2.96	-0.3

Table 1: Results of 6 resist formulations with resultant dose-to-size and LCDU changes

Figure 3: Impact of resist sensitivity on LCDU of p40 hexagonal pillars

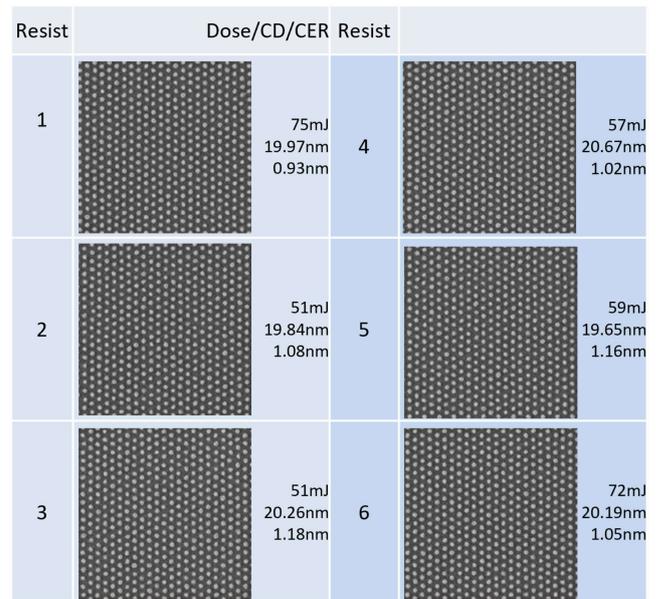


Figure 4: Images of pillar patterning using MTR resist with varying formulation ratios

decreasing LCDU with increasing dose for both 20nm and 23nm pillars. Figure 4 shows example CD SEM images of the pillars at 20nm diameter for the varying resist formulation ratios.

### 3.3 Generation 2 MTR resist – increasing sensitivity

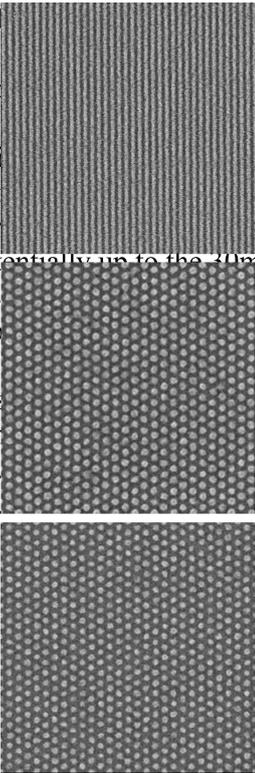
The MTR resist using XL-A and PAG1 has been used to pattern pitch 28nm lines using a film thickness of 20nm as seen in figure 2. We also present here high resolution images using a 17nm

Figure 5 Patterning using MTR Pilot resist using XL-A. From Top to Bottom: p24 line/space (rectangular image), Dose 52.5mJ/cm<sup>2</sup>, CD 11.3nm, p36 hex pillars, Dose 75.5mJ/cm<sup>2</sup>, CD 21.0nm; p34 hex pillars, Dose 80mJ/cm<sup>2</sup>, CD 17.5nm

film thickness. In figure 5, we present pitch 24nm lines with a CD of 11.3nm (as measured via the CD SEM program) and patterned at 52.5mJ/cm<sup>2</sup>. We also present p36 and p34 hexagonal pillars with a dose of 75.5 -

80mJ/cm<sup>2</sup>. However, there is always interest in decreasing the dose required for EUV resist to improve productivity, therefore research continues to try to maintain state of the art resolution of the resist whilst increasing the sensitivity for increased throughput capability. Initial results for MTR Gen 2 resist, see figure 6, show that by carefully

controlling the reactions in the CROP enable... with a sub 20mJ/cm<sup>2</sup> dose... thickness at pitch 28nm... will continue to reduce the... The tunability of the MTR... section 3.2, will allow for... slightly increase the dose, potentially up to the 40mJ/cm<sup>2</sup> level, with a probable... has also been research into... compared to PAG1. A... 6, using a 17nm film thickness... diameter pillars at pitch 34nm... of 19nm, with a dose of 27... be patterned successfully.



hexagonal with a dose of 80mJ/cm<sup>2</sup> to achieve 17.5nm diameter pillars. The tunability of MTR resist by changing the ratio of the components has been demonstrated with a 33% reduction in dose to size achieved with a concurrent increase in LCDU is 14%. Research continues to try to maintain state of the art resolution of the resist whilst increasing the sensitivity for increased throughput capability we have introduced high photospeed approaches, where we have patterned p28 lines and p34 hex pillars at sub-30 mJ/cm<sup>2</sup> doses.

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	p28		p34
dose 18.0mJ/cm <sup>2</sup> Line width 11.1nm		dose 27.75mJ/cm <sup>2</sup> Diameter 18.7nm	
dose 19.0mJ/cm <sup>2</sup> Line width 11.8nm		dose 28.25mJ/cm <sup>2</sup> Diameter 19.0nm	
dose 20.0mJ/cm <sup>2</sup> Line width 12.5nm		dose 28.75mJ/cm <sup>2</sup> Diameter 19.5nm	

Figure 6: Patterning using MTR Gen 2 Resist using XL-A showing p28 patterning at 20mJ/cm<sup>2</sup> and less; and p34 pillar patterning at sub 30mJ/cm<sup>2</sup>

#### 4. Conclusion

MTR Resist is a negative tone resist with dose dependent behaviour which can pattern high resolution patterns with EUV lithography. In this study we have shown Pitch 28nm dense patterns can be patterned at a dose of 59mJ/cm<sup>2</sup>, a line width of 12.5nm, and a biased LWR of 3.91nm. These resist formulations have also been used to pattern 20nm diameter pillars on a hexagonal 40nm pitch with a dose of 51mJ/cm<sup>2</sup>, and a CDU of 3.5nm; and also pillars at pitches of 34nm

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