Multi-Trigger Resist for EUV lithography

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Irresistible Materials (IM) is developing a photoresist based on the multi-trigger concept, which is designed to suppress roughness using a new photoresist mechanism incorporating a dose dependent quenching-like behaviour, and which is based on high EUV absorbance molecular, rather than polymeric, materials to maximise resolution. The latest results using the NXE Scanner are discussed here. The second generation (MTR Gen 2) of MTR incorporates more optimised crosslinker and photoacid generator molecules to tune the reaction rates in the multi-trigger mechanism. We have shown that the dose requirement compared to the first generation (MTR Gen1) of high opacity MTR resists previously presented can be significantly reduced without detriment to LWR or resolution. Lines and Spaces at p28 nm can be patterned at doses from 20 mJ/cm^2 to 50 mJ/cm^2 dependent on formulation ratio, with optimum LWR (3.95 nm, biased) occurring at 32 mJ/cm^2, CD 12.1nm, in a MTR Gen2.4 formulation. Similarly, we present p34 & p36 pillars patterned between 20 mJ/cm^2 and 60 mJ/cm^2 doses for 17 nm diameter pillars, with a minimum LCDU for 18 nm diameter p36 pillars of 3.6 nm at 45 mJ/cm^2 (MTR Gen2.4).

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

1. Introduction

Work is ongoing to develop a photoresist that supports the implementation of EUV lithography, and particularly high-NA EUV lithography, with increased focus on novel photoresist mechanisms. As traditional chemically amplified resists (CAR) are expected to reach a performance plateau with respect to low-Z-factor and low defectivity in high-NA, the development of alternative approaches materials becomes necessary. [1–3]

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. But the move to secondary electron chemistry allows for new approaches to be developed. However, the mechanism of low energy electron interaction with resist molecules are not yet entirely clear and further work to elucidate 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], or internal excitation of the photoacid generator by the secondary electron leading to a photolysis-like behaviour. [4,7]

The interface between the resist and the substrate is also affects the performance of the resist. The interaction of the resist with the underlayer can enhance or degrade performance, for instance by modulating the resist adhesion, whilst the generation of secondary electrons in the underlayer may also be important, and thus the chemical and physical properties of the underlayer should be carefully considered. [8,9] Furthermore the underlayer choice can also affect the metrology contrast in non-intuitive ways. [10]

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 increase, whilst ever thinner photoresists will also introduce pattern transfer challenges. [14]

The Multi-Trigger Resist (MTR) is a new platform under development by Irresistible Materials to address the on-going requirements of EUV lithography. MTR is a molecular resist, using a ring-opening polymerization (ROP) mechanism, which additionally includes a unique dose-dependent self-quenching mechanism, known as the multi-trigger mechanism, directly in the chemical pathways, to improve performance. The intrinsic self-quenching mechanism of MTR, which has been described before [15–21] provides an advantage in acid diffusion mitigation and offers a benefit on achieving ultimate resolutions with low line edge roughness.

After the development of the initial prototype of the resist, a high-EUV opacity variant was developed (MTR Gen1). This incorporates non-metal organic high-opacity moieties to improve the capture of EUV photons. XRR Measurements (CXRO) have shown that the absorption can be widely tailored. The prototype (low-opacity) MTR has an absorbance of ~6 μm^{-1}, whilst MTR Gen1 has demonstrated that the absorbance can be tuned between 12 and 18.2 μm^{-1}. Synthesis of even more highly functionalized molecules has been achieved, and projecting from the XRR measurements, it can be calculated, using the CXRO method, [22] that absorbances of 20–25 μm^{-1} could be achieved if required. MTR Gen1 is additionally a high-carbon content material with a low Ohnishi number, and shows low post development film thickness loss (~10%), to improve pattern transferability.

The second-generation of the MTR (MTR Gen2) focuses on optimisation of the reaction pathways of the high-opacity platform. [19] It was demonstrated that good lithographic performance for P28 L/S could be achieved with doses below 20 mJ/cm^2, whilst for hexagonal pillars P36 and P34 were patterned at doses as low as 30 mJ/cm^2. [23,24]

A number of different approaches to optimisation of the chemistry exist, and we have examined three separate routes to significantly improve the MTR Z-factor: by increasing the monomer activation rate (MTR Gen2.1); adjusting the relative ROP initiation and propagation reaction rates (MTR Gen2.2); and by improving the selectivity of the multi-trigger quenching mechanism (MTR Gen2.3). [25]

Here we present further results of the MTR Gen2.1 approach, together with initial results for MTR Gen2.2 & 2.3. In addition, we have examined whether the advantages gained by each approach are independent and show first indications that combining approaches 2.1 and 2.2 lead to further improvements (MTR Gen2.4).

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. Use of other underlayers has been described elsewhere. [25] After spin-coating of the resist using a track, samples received a post application bake (PAB) of 80°C for 1 minute, and were 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.

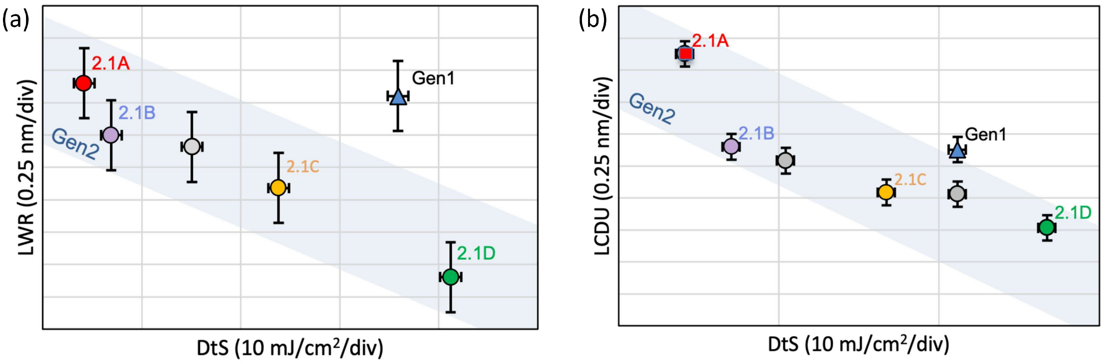


Fig. 1. Comparison in dose range and roughness between MTR Gen1 and MTR Gen2.1. (a) LWR as a function of dose-to-size for MTR Gen2.1 variants (compared to MTR Gen1) for p 28 lines and spaces; (b) LCDU as a function of dose-to-size for MTR Gen2.1 variants (compared to MTR Gen1) for p36 hex pillars. All exposures undertaken on the NXE3400, and with otherwise identical patterning and processing conditions.

3. Results

3.1 Optimisation of MTR Gen2.1 for p28 lines and spaces and p34 & p36 pillars

The optimisation of the MTR Gen2 resists provide a significant performance improvement over MTR Gen1. Fig. 1 shows the LWR as a function of dose-to-size of several formulations of MTR Gen2.1 compared to MTR Gen1. It can be seen that the effect is more marked for p28 line and space (L/S) patterning (Fig. 1 (a)), than for p36 pillars (Fig. 1 (b)). The flexibility of the MTR platform, whereby it is possible to optimise towards either speed or roughness, by varying the relative ratios of the MTR components is maintained in MTR Gen2.

Representative images of P28 L/S and P36 pillars obtained using the fastest formulation of the MTR MTR Gen2.1 series (MTR Gen2.1A) are shown in Fig. 2. The film thickness (FT) for L/S was 20 nm and for pillars the resist FT was 21.5 nm. The dose for L/S was 19 mJ/cm^2 and for pillars 29 mJ/cm^2.

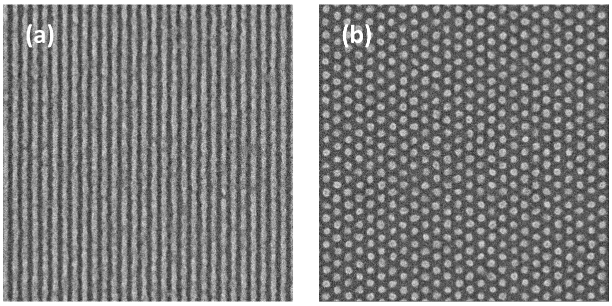


Fig 2. p28 L/S and p36 hexagonal pillars patterning in MTR Gen 2.1A; (a) Lines: CD 13.1 nm, dose 19 mJ/cm^2; (b) Pillars: CD 18.9 nm, dose 29 mJ/cm^2. Exposed using the NXE3400.

Whilst the MTR Gen2.1A can clearly resolve at the indicated pitches, the roughness is quite high. Due to the tunability of the MTR formulation, the roughness can be modulated relatively easily through formulation changes. MTR Gen2.1B, C, and D, have reduced sensitivity compared to MTR Gen2.1A but roughness and resolution improve.

Fig. 3 shows p34 hexagonal pillars patterned on the NXE3400 using MTR Gen2.1B, C, and D which have incrementally higher dose-to-size. The diameter of the pillars is 18 nm, and the doses are 35 mJ/cm^2 for MTR Gen2.1B, 55 mJ/cm^2 for MTR Gen2.1C and 76 mJ/cm^2 for MTR Gen2.1D.

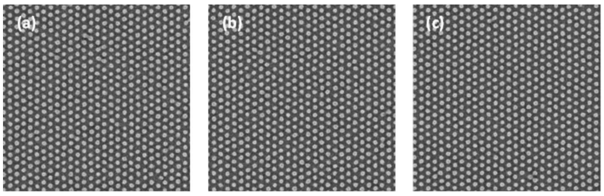


Fig 3. Hexagonal pillars of CD 18 nm patterned on the NXE3400 at p34: (a) MTR Gen2.1B, dose 35 mJ/cm^2; (b) MTR Gen2.1C, dose 55 mJ/cm^2, and (c) MTR Gen2.1D, dose 76 mJ/cm^2.

For p28 lines and spaces, the same trend is observed with roughness reducing from MTR Gen2.1B to D, with the doses used to obtain these patterns ranging from 25 to 59.5 mJ/cm^2, Fig. 4. The CD for these p28 lines is 13.8 nm, and all exposures were performed on the NXE3400.

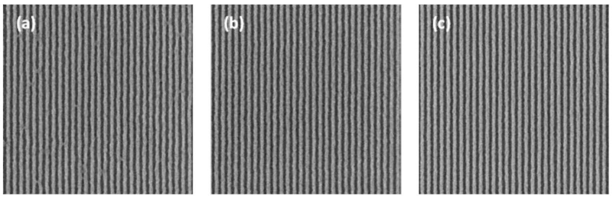
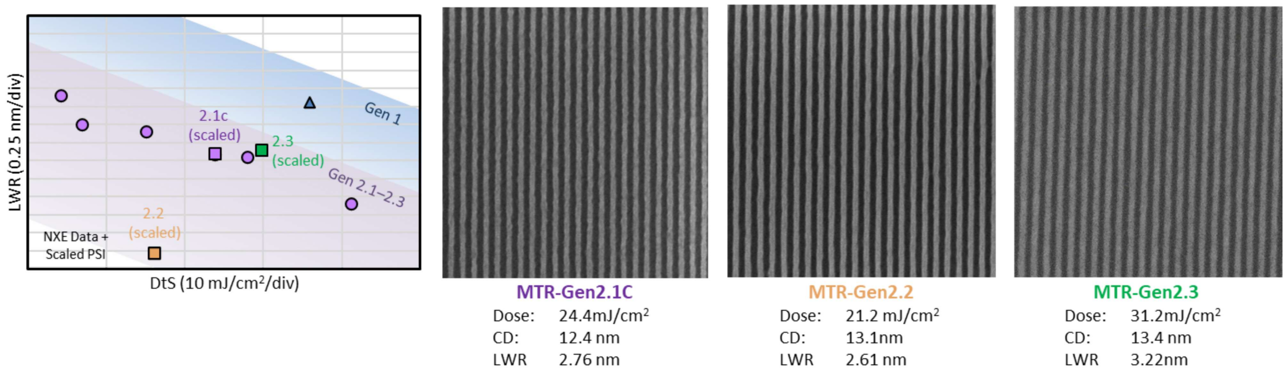


Fig 4. Lines and spaces of CD 13.8 nm patterned on the NXE3400 a p28: (a) MTR Gen2.1B, dose 25 mJ/cm^2; (b) MTR Gen2.1C, dose 42.5 mJ/cm^2; and (c) MTR Gen2.1D, dose 59.5 mJ/cm^2.

Fig. 6, p28 dense lines and p36 hex pillar patterned with MTR Gen2.4 resist



MTR-Gen2.1C
Dose: 24.4mJ/cm^2
CD: 12.4 nm
LWR 2.76 nm

MTR-Gen2.2
Dose: 21.2 mJ/cm^2
CD: 13.1nm
LWR 2.61 nm

MTR-Gen2.3
Dose: 31.2mJ/cm^2
CD: 13.4 nm
LWR 3.22nm

Fig. 5. Lines and space patterned at P28 at PSI for MTR Gen2.1C, MTR Gen2.2 and MTR Gen2.3. Each has a different optimisation strategy, and all three out-perform MTR Gen1.

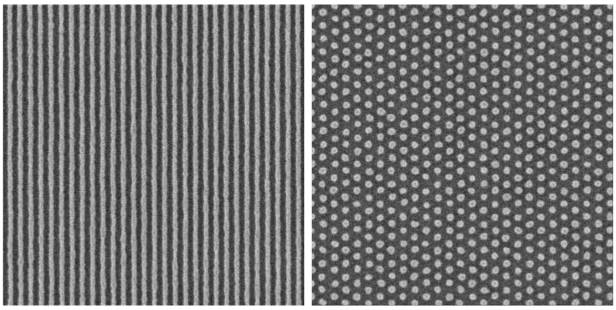
3.2 Results for MTR Gen2.2 – Gen2.3

Evaluation of MTR Gen2.2 optimizations (improved polymerization) and MTR Gen2.3 approaches (better termination selectivity) was undertaken at PSI. As with MTR Gen2.1 both approaches to enhancing the performance of the MTR system show performance improvement over MTR Gen1 as shown in Fig. 5.

3.3. Introducing MTR Gen 2.4

For each of MTR Gen2.1 – 2.3 the optimizations addressed a single aspect of the MTR chemical mechanism to improve performance. MTR Gen2.4 takes the improvements seen in MTR Gen2.1 and MTR Gen2.2 and combines them.

Initial results from imec patterning for MTR Gen2.4 shows that additional benefits come from the simultaneous optimization of two reaction mechanisms. Fig. 6 shows p28 lines patterned at 32mJ/cm^2 to achieve a line width of 12.1nm with a biased LWR of 3.95nm, and a p36 hexagonal array of pillars patterned at 45mJ/cm^2 with a pillar diameter of 18.3nm and an LCDU of 3.6nm. Compared to previous formulations, the MTR Gen2.4 achieves the same p28 biased LWR as MTR Gen2.1 with a 40% reduction in dose.



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 second-generation MTR formulations was shown. The fastest variant of MTR Gen2.1 was 3 times faster than MTR Gen1, with only a very small increase in LWR in L/S patterning, whilst sensitivity could be doubled for hexagonal pillar patterning whilst maintaining LCDU. MTR Gen2.1 optimizes the monomer activation rate; similar performance enhancement is seen by optimizing the ROP reaction rates (MTR Gen2.2 [20]), or improving the multi-trigger efficiency (MTR Gen2.3; Fig. 5). These performance gains appear to be non-correlated and MTR Gen2.1 & 2.2 can be combined to achieve further improvement (MTR Gen2.4; initial NXE3400 data Fig. 6).

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