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ABSTRACT

Irresistible Materials is developing a new molecular resist system that demonstrates high-resolution capability based on the multi-trigger concept. A series of studies such as resist purification, developer choice,and enhanced resist crosslinking were conducted in order to optimize the performance of this material. The optimized conditions allowed patterning 14 nm half-pitch (hp) lines with a line width roughness (LWR) of 2.7 nm at the XIL beamline of the Swiss Light source. Furthermore it was possible to pattern 14 nm hp features with dose of 14 mJ/cm^2 with an LWR of 4.9 nm. We have also begun to investigate the addition of high-Z additives to EUV photoresist as a means to increase sensitivity and modify secondary electron blur.

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

1. INTRODUCTION

EUV lithography (EUVL) is considered to be one of the most promising candidates to replace current 193 nm photolithographic tools for future semiconductor manufacturing needs. A wide array of new materials have been introduced to support the new technology [1–3], but to date no photoresist has been able to simultaneously meet resolution, linewidth roughness and sensitivity (RLS) requirements laid out in the International Technology Roadmap for Semiconductors. In addition to fulfilling the current resist targets for the next generation of devices; new material platforms must also have the potential to meet the outlined specifications beyond that point, to ensure a useful lifespan for next generation lithography. Traditional chemically amplified (CAR) materials have been extended to try and meet this need, but as resolution improvements have led to significant sensitivity reductions, with typical CAR dose to size in the 30 – 40 mJ/cm2 range at 14 nm halfpitch (hp). [4,5] In order to increase absorption of EUV photons metal-based resist materials have been heavily investigated and significant work to try to alleviate industry apprehension about the integration of metal resists in to fab-friendly processes undertaken. Doses of less than 25 mJ/cm^2 at 16 nm halfpitch and 35 mJ/cm^2 at 13 nm hp have been reported. [6] Increasingly industry is calling for new approaches and more radical chemistries to address the RLS issue. An investigation of metal additives to traditional chemically amplified resist to increase optical density has shown increased sensitivity in contact hole patterning from 50 to 43 mJ/cm^2 for 22 nm halfpitch contact holes, but at the cost of increased variability in the hole size [7]. The PSCAR process which uses a

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flood UV exposure to amplify the acid produced via an earlier EUV exposure has demonstrated significant reductions in dose requirement from 30 mJ/cm^2 at 18 nm hp to 17 mJ/cm^2 but with a significant reduction in exposure latitude and increase in LWR also reported. [8].

Irresistible Materials is developing a negative tone molecular resist platform, known as xMT, for EUVL applications. The xMT resist demonstrates a good combination of photo speed, low line edge roughness (LER) and high-resolution patterning [8]. Existing state-of-the-art photoresists are based on the concept of chemical amplification (Chemically Amplified Resists, or CARs), wherein each incoming photon causes multiple chemical reactions within the resist, significantly improving sensitivity. However, the amplification process is unconstrained and leads to blurring at the edge of features, reducing the achievable resolution and limiting LER performance. A variety of methods can be used to control the amplification, and improve resolution, such as the addition of base additives at low concentrations. However, these typically reduce the performance of the resist, for instance impacting on the dose, or increasing the LWR because of material stochastics. Irresistible Materials has developed a new category of resist chemistry that addresses these limitations called 'Multi-Trigger Resists'. In a Multi-Trigger resist, multiple distinct chemical reactions must take place simultaneously and in close proximity for the amplification process to proceed. Thus, at the edge of a pattern feature, where the density of photo-initiators that drive the chemical reactions is low, the amplification process ceases. This significantly reduces blurring effects and enables much improved resolution and line edge roughness while maintaining the sensitivity advantages of chemical amplification.

Here we report our ongoing efforts to optimize the formulation to further improve the performance of this material. As the patterning dose of resists typically increase as the feature size decreases we have also begun to explore the addition of metal containing compounds to our resist that ideally do not impact the pattern quality while improving the sensitivity and results are presented here.

2. EXPERIMENTAL

The resist samples were prepared by dissolving the individual components in ethyl lactate. They were then combined in various weight ratios and concentrations. The resist was spun onto a proprietary carbon underlayer that we have developed consisting of a mixture in equal parts of a fullerene derivative and an epoxy crosslinker. Prior to the application of the underlayer the silicon substrates were cleaned in a three-step process: 10 min immersion in isopropyl alcohol (IPA) in an ultrasonic bath, 10 min immersion in piranha solution (1:1 H_2SO_4:H_2O_2) and finally 2 min dip in a weak aqueous solution of hydrofluoric acid (0.1-1%).

After spin coating of the resist the samples received a post application bake. All EUV exposures were performed using the XIL-II interference lithography tool at the Paul Scherrer Institute, Switzerland [10]. After exposure the samples received a post exposure bake and were developed in n-butyl acetate for 60 seconds followed by an MIBC rinse.

Exposed samples were analyzed with a scanning electron microscope (SEM) in top-down view. Critical dimension (CD) and LER were calculated from the SEM images with the commercial software package SuMMIT. As the XIL tool does not allow direct measurement of the dose at the wafer, the exposure was measured with respect to an internal PSI reference resist calibrated against exposures of the same resist at the Intel MET [11]. For features smaller than the capability of the calibration resist, dose was estimated from higher pitch sizes.

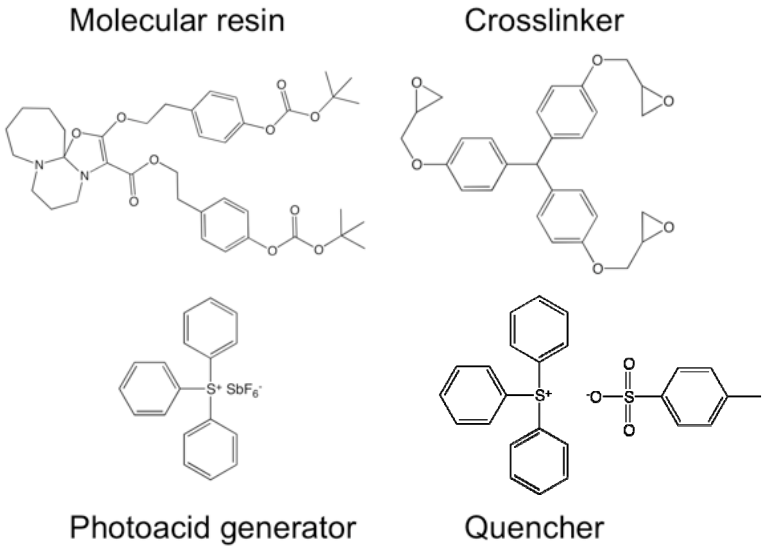

Figure 1 Baseline resist components of xMT resist

3. RESULTS

The baseline material for the optimization efforts is the previously introduced xMT resist [12]. It is a blended formulation of xMT resin, molecular epoxy crosslinker and a sulfonium photoacid generator mixed in 0.2:2:1 weight ratio with the addition of a quencher in the form of a photo-decomposable nucleophile that controls epoxy crosslinking [13,14]. The chemical structures of the components are shown in figure 1.

3.1 Resist Optimization

Recent work has been undertaken to improve resist purity of all components to SEMI specifications. We have used Zeta Plus 40Q purifier cartridges from 3M Purification Inc, which are high capacity purifiers designed to remove metallic ion contaminants from high purity chemicals such as resins, photoresists, and solvents. The purifier contains ion exchange groups that have been bonded within a porous depth media structure. This construction enhances surface area for the ion exchange groups assuring metallic contaminant removal to single digit ppb levels. The process, as shown in figure 2, significantly reduces the amount of contaminant metals such as sodium, calcium, chromium, and magnesium. EUV exposures have been undertaken before and after purification, using the XIL beamline of the Swiss Light source at the Paul Scherrer Institute [10]. High resolution patterning at 14 nm halfpitch (see figure 3) and 16 nm halfpitch showed that the purified formulation, with removed contaminants, was significantly more sensitive than the standard formulation (see figure 4). The dose required for the optimized resist when no quencher is added is 64% that of the standard formulation with no quencher. The dose required for the optimized resist with quencher is 77% that of the standard formulation with quencher. The line edge roughness of the lines is improved by over 10% using a separately purified quencher in conjunction with the optimized xMT and crosslinker, compared to the standard formulation (see figure 5). The production of resist with less contamination therefore has significant performance benefits. Even at relatively low levels, the contaminants have been interfering with multiple distinct chemical reactions within the multi-trigger resist, effectively quenching the process.

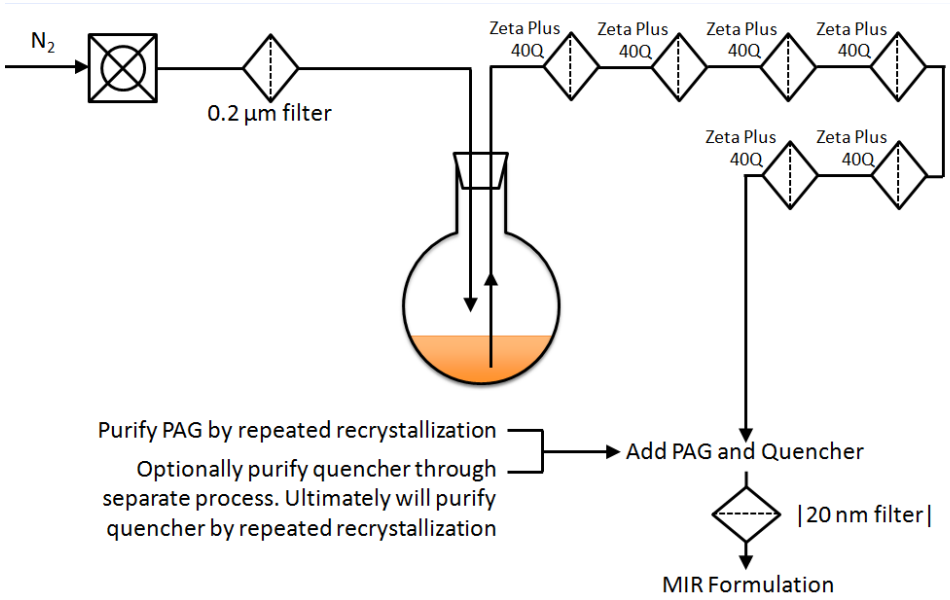

Figure 2 Schematic of purification procedure

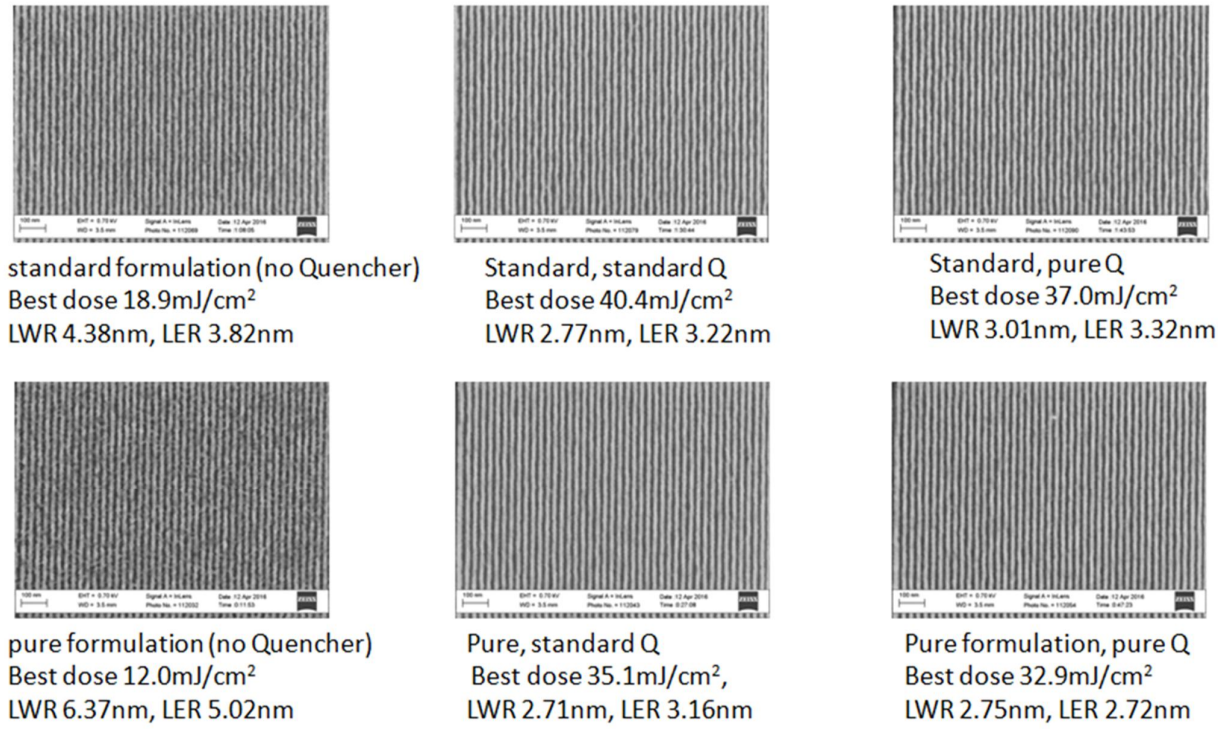

Figure 3 SEM of 14nm hp lines showing sensitivity and dose improvement with purification

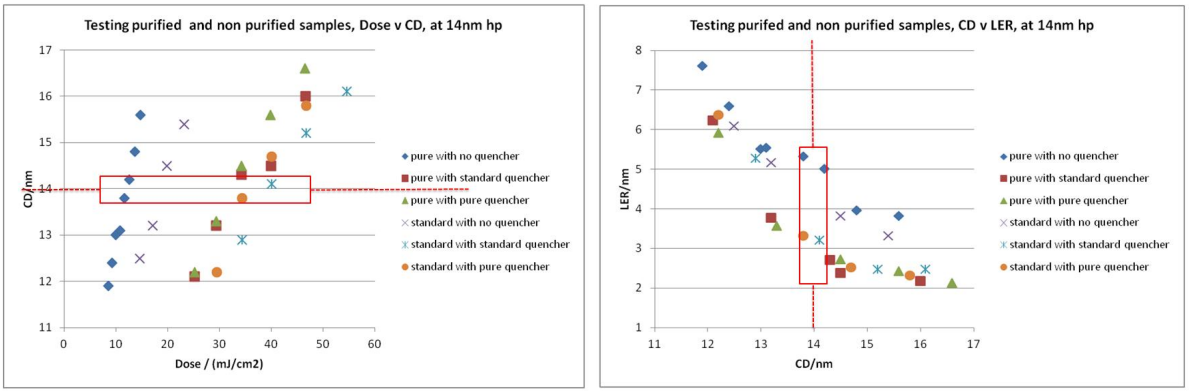

Figure 4 Sensitivity and LER changes with purification of resist

3.2 Developer choice

The choice of developer for a resist system has always been a key process variation, which can influence particularly the roughness of the patterning [15]. We took a resist formulation, the non-purified version with 2.5% quencher loading, then processed and exposed the samples in consecutive exposure runs, with identical conditions, except for the choice of developer. The results in figure 5 show that the choice of developer does make a big difference to the 'dose to size', probably due to the effect that the developer has on the swelling of the lines during the development stage. Figure 6 shows that ethyl acetate and benzyl acetate have the same or slightly better LER than n Butyl Acetate (nBA), and the lines are slightly narrower at a set dose (the resist is slightly less sensitive). Ethyl acetate could give an advantage in LER at high resolution particularly, but there may be a 6% dose increase compared to nBA. Octyl acetate and tert-butyl acetate appear to cause more swelling - the lines are thicker at a set dose (the resist appears more sensitive), but the LER is worse.

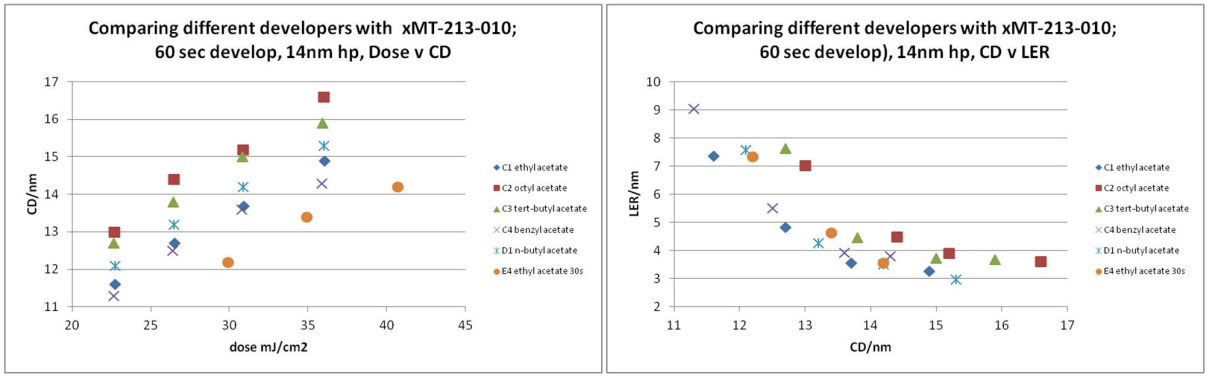

Figure 5 Showing sensitivity and LER changes with different developers

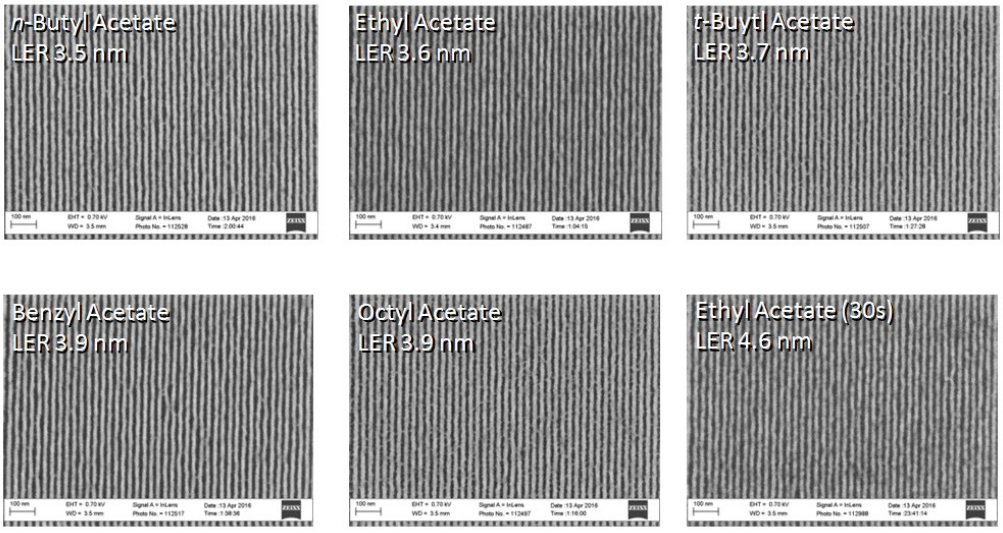

Figure 6 SEMs showing LER changes with different developers at 14nm half pitch

3.3 Enhancement to base molecular resin

We also present enhancements to the base molecular resin itself, seen in figure 1. One variant, EX1, includes additional functional groups designed to increase sensitivity, whilst another variant, EX2, is designed to stiffen the molecule to reduce line edge roughness. Results are again presented from exposures at PSI. The formulation is non-purified and uses 2.5% quencher addition. The EX1-213-010 variant exhibits a significant sensitivity improvement of around 25% with similar LER values as xMT-213-010 (see figures 7 and 8). The EX2-213-010 variant exhibits improved LER values especially at half pitches below 16nm, with a 20% LER improvement at 14nm hp, giving an LER of 2.7nm at 14nm (see figures 7 and 8). It is expected that when a purified version of these results are patterned, the sensitivity will increase by around 20% as seen with the base XMT version, and future exposures will use a purified version.

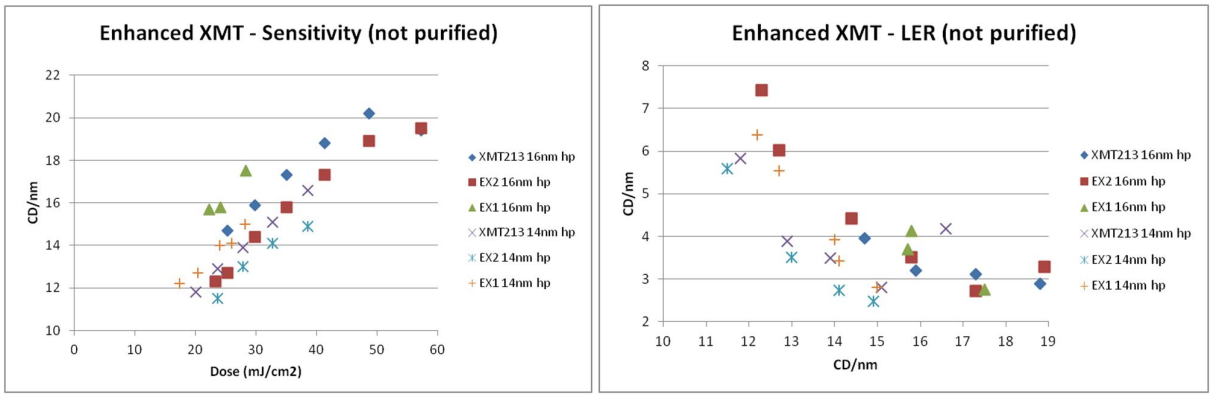

Figure 7 Effect of using enhanced XMT molecules on sensitivity and LER

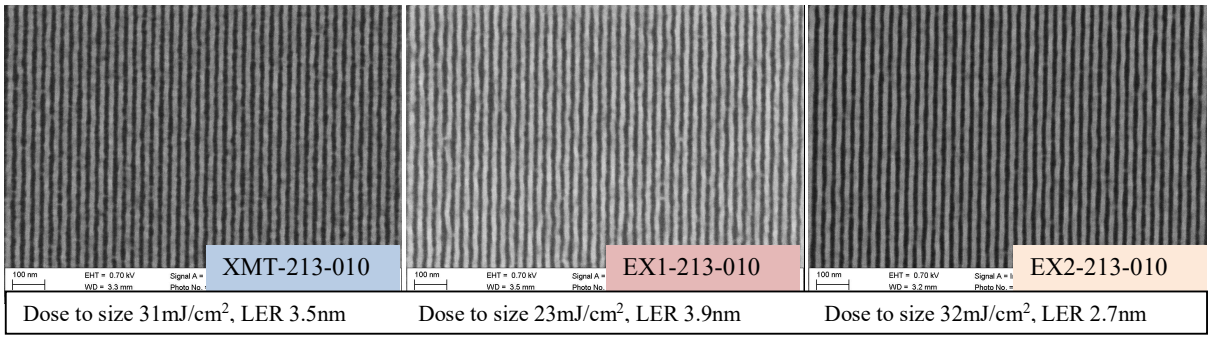

Figure 8 SEM images of 14nm hp lines showing improvement in sensitivity and LER

3.4 High-Z Additives

Metal-based resists are currently receiving much attention. Metals often have a higher absorption at 13.5 nm wavelength radiation compared to organic resist materials, primarily due to their higher Z number.[16] Higher absorption is a potential route to overcome the photon shot noise limit in EUV lithography as well as significantly improve sensitivity to enable high volume manufacturing at current source power output. While many efforts focus on the higher absorption properties of metals, there is another aspect to high-Z materials as well. Fundamental studies are currently under way about the different nature of light-resist interaction in the EUV range, but electron scattering properties are thought to be an important part of this. For example they account for the secondary electron blur. Therefore we devised the concept of high-Z additives, chemical compounds that contain the species of interest that are blended into the xMT resist, to create a hybrid resist. In a first instance this concept is shown as a sensitizer to increase the sensitivity of the xMT but in further work we intend to screen for the differences in resist – electron interaction as well. So far we have tested about 20 different high-Z sensitizers including both metal containing and non-metal containing additives, and seen a variety of different behaviours with the high-Z addition both increasing or decreasing the sensitivity depending on the choice. In figure 9, for the 3 different hybrid versions (named HB1, HB2 and HB3) a metal containing sensitizers was added. The metal has been kept identical in all three cases, with the same metal weight being added into the formulation, and the ligand, which the metal is attached to, has been changed. This shows that the ligand choice is key to the outcome of sensitivity, with some producing a resist requiring a 5% higher dose, whilst others improved the sensitivity by over 20%. However, when patterning 16nm hp and 14nm hp lines at PSI, the LER values are all increased compared to the standard xMT version of the resist.

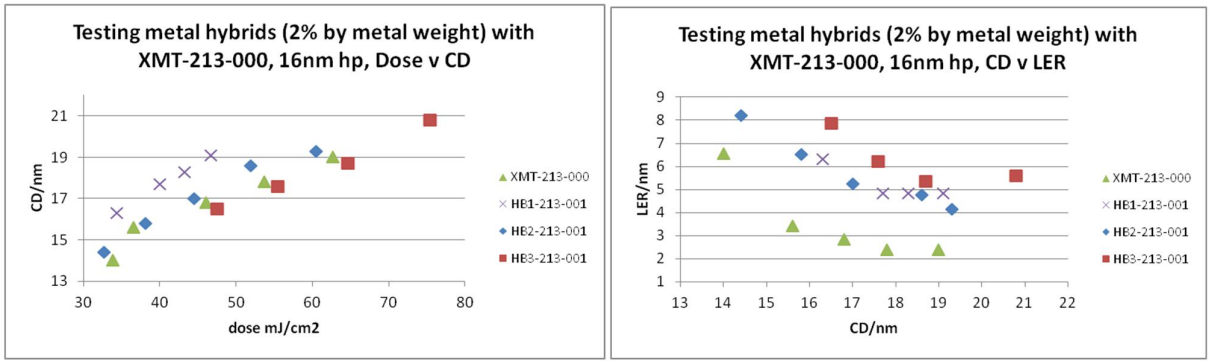

Figure 9 Changes in sensitivity and LER with added metal

4. CONCLUSION

We have undertaken a series of studies to optimize the performance a negative tone molecular resist platform.

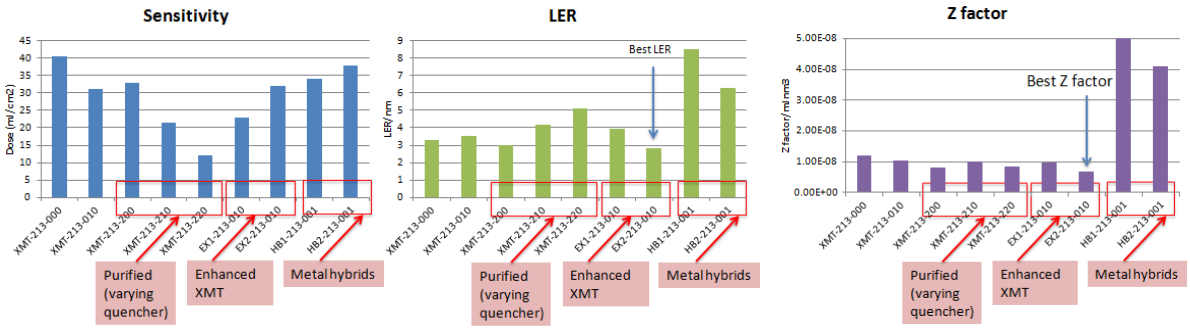

Figure 10 Performance of tested resist formulations at 14nm half pitch

Whilst a dose of less than 25mJ/cm^2 can be achieved with a number of formulations, i.e. by eliminating the quencher entirely (xMT-213-220), or by purifying a low quencher version (xMT-213-210), or by using a modified xMT version (EX1-213-010), the LER values in these 3 instances are around 4.0 nm or over. Adding metal to the resist system (HB1-213-001 and HB2-213-001) gives a sensitivity enhancement (directly compared to xMT-213-000), but the LER increase and subsequent Z factor increase do not indicate that this resist system will give us the optimal results when patterning at PSI. The best overall resist comes in the second version of the modified xMT molecule, EX2-213-010, which was designed to improve LER by stiffening the molecule. Future work will investigate using a purified version of an enhanced xMT resist combining the sensitivity improvements of EX1 with the LER improvements of EX2, with the aim of incorporating the performance improvements illustrated into one system, which will have a sub 20mJ/cm^2 dose with a sub 3nm LER.

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