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Abstract. With extreme ultraviolet lithography (EUVL) emerging as one of the top contenders to succeed from optical lithography for the production of next generation semiconductor devices, the search for suitable resists that combine high resolution, low line edge roughness (LER) and commercially viable sensitivity for high volume production is still ongoing. One promising approach to achieve these goals has been the development of molecular resists. Here we report our investigations into the EUV lithographic performance of a molecular fullerene resist showing resolution down to 20-nm half-pitch with interference lithography with a LER of >5 nm and sensitivity of about 20 mJ/cm². © The Authors. Published by SPIE under a Creative Commons Attribution 3.0 Unported License. Distribution or reproduction of this work in whole or in part requires full attribution of the original publication, including its DOI. [DOI: 10.1117/1.JMM.12.3.033010]

Subject terms: extreme ultraviolet lithography; molecular resist; fullerene; chemically amplified resist.

1 Introduction

With the advancement in next generation lithography (NGL) technology continuing, the progress in patterning capability is increasingly being limited by the lithographic performance of the photoresist. Current lithographic nodes already require line width roughness that is smaller than the radius of gyration of typical resist polymers. Further progress in the development of new resists is needed to enable the commercial production of semiconductors at the sizes mapped for the future. Low molecular weight resists, such as fullerenes, triphenylenes, molecular glasses, and inorganic resists, have been a focus of interest for NGL because their small size promises high resolution and small line edge roughness. But so far, no resist candidate has emerged that fulfills all the industry’s criteria.

We have previously reported on the performance of a fullerene derivative based three-component negative tone chemically amplified resist for e-beam lithography with low line edge roughness (LER) and high resolution capability, and on a positive tone variant of the fullerene resist. E-beam resists have often been shown to work in extreme ultraviolet lithography (EUVL) as well because of similarities in the exposure mechanisms in the resist. Therefore, we believe that this resist platform has a great potential for EUVL. Here we present recent results of our investigation into the EUVL performance of a fullerene derivative based resist system.

2 Experimental Methods

Fullerene derivatives for the resist were supplied by Irresistible Materials Ltd., United Kingdom Figure 1(a) shows the tert-butoxycarbonyl (tBOC) protected methyl phenolic malonate C₆₀ derivative (IM-MFPT-12-21), and the tBOC protected propyl phenolic malonate C₆₀ derivative (IM-MFPT-12-8, -12-19, -13-32, -13-33). An epoxy
crosslinker (Araldite ECN 1299; Huntsman Advanced Materials, The Woodlands, Texas) [Fig. 1(c)] and triphenyl-
sulfonium hexafluoroantimonate PAG (TPS-103; Midori
Kagaku Co., Japan) [Fig. 1(d)] were added.

Synthesis of the derivatives was achieved via the modified
Bingel cyclopropanation reaction of a bismalonate
ester, with the \( \text{C}_{60} \), to afford the methanofullerenes and is
described in depth elsewhere (Yang et al., unpublished).

2.1 IM-MFPT-12-8

In a round bottom flask, \([\text{60}]\text{fullerene} (1 \text{ equivalent})\), \(9,10\)-dimethylxanthracene (22 equivalent) and toluene were
added. The resulting solution was stirred for 1 h to completely
dissolve the fullerene. Carbon tetrabromide (22 equivalent) and 3-(4-\(t\)-butoxycarbonyl)phenyl-1-propyl malonate (22 equivalents) were added to the solution. 1,8-Diazabiclo[5.4.0]undec-7-ene (DBU) (108 equivalents) was added dropwise and the resulting mixture was stirred
at room temperature overnight and the initial purple solution
had become a dark red color. The crude mixture was poured
through a silica gel plug in a sintered glass funnel and rinsed
with toluene to remove unreacted \([\text{60}]\text{fullerene} \). After that, the plug was rinsed with dichloromethane:ethyl acetate:methanol (2:2:1) to remove the red/brown band contain-
ing the crude products. The filtrate was evaporated and the resulting residue was purified via flash column chromatography with dichloromethane:ethyl acetate:methanol as eluent. (\(t\)-butoxycarbonyl malonate)-methano-[\text{60}]fullerene (1.8 g, dark red/brown oil) was obtained. The oil was dissolved in methylene chloride at a concentration of 65 g/L
and processed by semi-preparative size exclusion chromatography (Phenogel SEC 300 x 7.8 mm, 5 \(\mu\)m particle size, eluent: methylene chloride, 4 mL/min). The material corresponding to 1000 to 3000 atomic mass unit (AMU) was collected and the solvent was evaporated to obtain a red oil. This material was characterized by MALDI MS.

2.2 IM-MFPT-12-19

IM-MFPT-12-19 was synthesized and purified as for IM-
MFPT-12-8. The crude mixture was redissolved in methyl-
ene chloride at a concentration of 65 g/L and processed by
size exclusion chromatography (Phenogel SEC 300 x 7.8 mm,
5 \(\mu\)m particle size, eluent: methylene chloride, 4 mL/min). The material corresponding to 1000 to 3000 atomic mass unit (AMU) was collected and the solvent was evaporated to obtain a red oil. This material was characterized by MALDI MS.

2.3 IM-MFPT-12-21

In an 1-L round bottom flask, \([\text{60}]\text{fullerene} (0.85 g, 1.2 \text{ mmol})\), \(9,10\)-dimethylxanthracene (2.62 g, 13 mmol, 11 equivalents) and toluene (500 mL) were added. The resulting solution was stirred for 1h to completely dissolve the fullerene. Carbon tetrabromide (4.78 g, 13 mmol, 11 equivalents) and \(t\)-butoxycarbonyl malonate (6.6 g, 13 mmol, 11 equivalents) were added to the solution. DBU (8.3 mL, 53.2 mmol) was added dropwise and the resulting mixture was stirred at room temperature overnight and the initial purple solution had become a dark red color. The crude mixture was poured through a silica gel plug in a sintered glass funnel and rinsed with toluene to remove unreacted \([\text{60}]\text{fullerene} \). After that, the plug was rinsed with dichloromethane:ethyl acetate:methanol (2:2:1) to remove the red/brown band containing the crude products. The filtrate was evaporated and the resulting residue was purified via flash column chromatography with dichloromethane:ethyl acetate:methanol as eluent. (\(t\)-butoxycarbonyl malonate)-methano-[\text{60}]fullerene (1.8 g, dark red/brown oil) was obtained. The material corresponding to 1000 to 3000 AMU was collected and the solvent was evaporated to obtain a red oil. This material was characterized by MALDI MS.

2.4 IM-MFPT-13-32 and IM-MFPT-13-33

They were synthesized for IM-MFPT-12-8. Reaction crude
mixture was poured through flash column chromatography
using silica gel and washed with toluene to remove unreacted

![Fig. 1](http://nanolithography.spiedigitallibrary.org/)

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[60] fullerene and then two bands were obtained with different eluents: dichloromethane: ethyl acetate (1:1) and dichloromethane: ethyl acetate:methanol (2:2:1). The solvents were evaporated and the resulting two residues (IM-MFPT-13-32 and IM-MFPT-13-33, dark red/brown oil) were obtained. $^1$H nuclear magnetic resonance (NMR) (IM-MFPT-13-32, 300 MHz, CDCl3): $\delta = 6.90$ to 7.70 (m), 0.9 to 4.1 (m), 1.55 (s). $^1$H NMR (IM-MFPT-13-33, 300 MHz, CDCl3): $\delta = 10.8$ (s), 6.90 to 8.70 (m), 0.9 to 4.1 (m), 1.55 (s). The products were also characterized by MALDI MS.

Silicon substrates of $18 \times 18$ mm$^2$ were prepared by dicing a 100-mm n-type, (100)-silicon wafer (Rockwood Electronic Materials, France) using a Disco DAD 321 wafer dicer. The substrates were cleaned using semiconductor grade chemicals (Puranal, Sigma Aldrich). After dicing, the substrates were immersed in isopropyl alcohol (IPA) and placed in an ultrasonic bath for 10 min. The samples were then rinsed in flowing deionized (DI) water for 1 min (Purite Neptune, 18.2 MΩcm) before being immersed in freshly prepared $\text{H}_2\text{SO}_4$ (95% to 98%): $\text{H}_2\text{O}_2$ (30%) [1:1] for 10 min. After another 1-min rinse in flowing DI water, the substrates were dipped for 3 min in a weak aqueous solution of hydrofluoric acid (0.1% to 1%) to form a hydrophobic surface, and finally a further 1-min rinse in flowing DI water. They were then dried with nitrogen and immediately coated with a fullerene containing underlayer, based on a thinned material towards improvement of mechanical stability to allow for higher aspect ratios.

EUV exposures were performed using the interference lithography tool at the Paul Scherrer Institute (PSI), Switzerland. $^{18}$ Solutions of resist were formulated at PSI by mixing the fullerene derivative with the crosslinker and photo acid generator at various ratios and concentrations, typically 1 part fullerene to 2 parts crosslinker and 1 part photoacid generator (PAG) by weight, in ethyl lactate or propylene glycol monomethyl ether. No other components (quencher etc.) were added. Resist was spun onto the substrates at 1000 to 2000 rpm for 60 s and received a postapplication bake of 75°C for 5 min. After the exposure, the samples were baked at 90°C for 3 min before being developed in monochlorobenzene (MCB):IPA [1:1] for 20 s followed by rinsing in IPA. Alternative developers, cyclohexanone and 2-heptanone, have also been used successfully, as discussed below.

Exposed samples were analyzed with a FEI XL30 SFEG 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. Dose at the wafer was calibrated for each exposure run by using a reference resist as detailed elsewhere. $^{16}$

### 3 Results and Discussions

The exposure of numerous variants of the resist formulation showed that it is capable of high resolution. Examples of resist patterns with half-pitches down to 20 nm are shown in Fig. 2. The corresponding resist metrics are summarized in Table 1. The images suffer somewhat from low contrast, which is due to the necessary thinness of the resist film. We found that for aspect ratios significantly greater than $\sim$1:1, the resist is prone to pattern collapse at half-pitches $>25$ nm. Nevertheless, there is a significant potential for improvement in the process of optimizing the synthesis of the fullerene material towards improvement of mechanical stability to allow for higher aspect ratios.

We observed that adopting thinner films seemed to introduce further roughening in the line edge, as would be anticipated from previous results. $^{19,20}$ Figure 3 shows two resist films patterned at 30-nm half-pitch. Figure 3(a) shows variant IM-MFPT12-19, spin coated from a 6.67 g/L propylene glycol methyl ether (PGME) solution at 1000 rpm to give a film thickness of 20 nm, given a postapplication bake of 75°C for 5 min, exposed to EUV at 20 mJ/cm$^2$, given a post-exposure bake of 90°C for 3 min and developed in MCB:IPA.

![Fig. 2 Exposed fullerene resists at (a) 30-nm hp, (b) 25-nm hp, (c) 22-nm hp and (d) 20-nm hp.](image-url)
Figure 3(b) shows a very similar variant, IM-MFPT12-8, which is known to be marginally less sensitive to EUV than IM-MFPT12-19. In this case, the film concentration was 10 g/L to give a film thickness of 40 nm, and the exposure dose was 30 mJ/cm², but conditions were otherwise the same. It can be seen that the LER is substantially higher in Fig. 3(a) than in Fig. 3(b). Therefore, increasing the resist thickness through improvement in the mechanical stability of the resist or pattern collapse mitigation should lead to improvement in LER at lower half-pitches.

The CD versus dose and LER versus dose behavior for a ~20-nm film of variant IM-MFTP12-21, exposed under the same conditions as IM-MFTP12-19 above are shown in Fig. 4(a) and 4(b), respectively. It can be seen that the LER is not significantly increased as the dose goes from 20 to 30 mJ/cm².

Sensitivity curves for two of the resist variants were also obtained by using an open frame with a square aperture rather than the metal gratings for exposure. From the curves shown in Fig. 5, it can be seen that depending on the synthesis conditions, the material shows a range of variation in sensitivity. Also illustrated is the effect on sensitivity when the two resist materials are used in combination by mixing them together. By adding together the low and high sensitivity materials, a resist with intermediate sensitivity is created.

Different developers were tested, as our traditional developer MCB is not acceptable in industrial usage. The exposed material was found to develop as well in 2-heptanone, or in

| Half-pitch | 30 nm | 25 nm | 22 nm | 20 nm |
|------------|-------|-------|-------|-------|
| CD         | 31.2 nm | 26.0 nm | 22.6 nm | 20.2 nm |
| LER        | 5.45 nm | 4.68 nm | 4.79 nm | 5.65 nm |
| Dose       | 20.5 mJ/cm² | 23.0 mJ/cm² | 25.2 mJ/cm² | 20.3 mJ/cm² |

Figure 3 Comparison of line edge roughness (LER) for (a) 20 nm (LER = 7.76 nm) and (b) 40 nm (LER = 2.05 nm) thick films.

Figure 4 (a) CD versus dose at two half-pitches, and (b) LER versus dose, for the IM-MFTP12-21 variant.

Figure 5 Fitted sensitivity curves for materials IM-MFTP13-32 and IM-MFTP13-33.
high etch resistance in plasma etching, 21 an important factor to reduce LER. Furthermore, they have been shown to have smaller molecule size that potentially helps to show the reverse characteristics with increased sensitivity at the expense of LER. This seems to suggest that 2-heptanone is a less aggressive developer with reduced solubility of the exposed resist material. The MCB lies on the middle ground in terms of resist performance with both sensitivity and LER lying in the range between the other two chemicals.

4 Conclusion
We have presented first results of the EUV exposure of a novel negative tone chemically amplified molecular fullerene resist. The use of fullerens as resist material is attractive as they have a small molecule size that potentially helps to reduce LER. Furthermore, they have been shown to have a high etch resistance in plasma etching, 21 an important factor as progress in lithography has made it necessary to reduce resist thickness. While it was initially surprising to see a tBOC protected phenol used in combination with an epoxy as a good negative tone resist, we have confirmed a significantly better performance than for the unprotected phenol variant of the phenolic fullerene. If the crosslinking component is removed, the negative tone behavior of the tBOC protected phenol is no longer observed, indicating that this is not a simple polarity switch. The mechanism of action is currently being elucidated using a model resist, but we speculate that the acid labile tBOC group is removed by the PAG-generated acid, with the epoxy reaction cationically catalyzed. Analysis of the lithographic performance of the fullerene resist has shown that it possesses resolution, and sensitivity within or close to the target values of the International Technology Roadmap for Semiconductors 22 for 2016, but further work is ongoing to reduce LER in the thin films required for high resolution.

Table 2 Resist metrics for different developers.

| Developer | MCB:IPA | 2-heptanone | cyclohexanone |
|-----------|---------|-------------|--------------|
| CD        | 22.3 nm | 21.9 nm     | 22.4 nm      |
| LER       | 6.52 nm | 3.63 nm     | 9.91 nm      |
| Dose      | 19.52 mJ/cm² | 29.83 mJ/cm² | 17.36 mJ/cm² |

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References
1. R. L. Brainard et al., “Resists for next generation lithography,” Microelectron. Eng. 61, 707–715 (2002).
2. F. P. Gibbons et al., “Fullerene resist materials for the 32 nm node and beyond,” Adv. Funct. Mater. 18(13), 1977–1982 (2008).
3. J. Manyam et al., “Chemically amplified fullerene resists for e-beam lithography,” Proc. SPIE 6923, 69230M (2008).
4. H. M. Zaid et al., “Chemical amplification of a triphenylene molecular electron beam resist,” Adv. Funct. Mater. 17(14), 2522–2527 (2007).
5. T. Tada et al., “A triphenylene derivative as a novel negative/positive tone resist of 10 nanometer resolution,” Microelectron. Eng. 53(1–5), 425–428 (2000).
6. R. A. Lawson, L. M. Tolbert, and C. L. Henderson, “Single component molecular resists containing bound photocarrier functionality,” Proc. SPIE 7273, 72733C (2009).
7. W. A. C. Bauer et al., “Concomitant optimization of a molecular glass photosensitive system for electron beam lithography,” Adv. Mater. 25(45), 5404–5408 (2011).
8. M. Trikeriotis et al., “A new inorganic EUV resist with high-etch resistance,” Proc. SPIE 8322, 83220U (2012).
9. J. K. Stowers et al., “Directly patterned inorganic hardmask for EUV lithography,” Proc. SPIE 7969, 796915 (2011).
10. J. Manyam et al., “Low activation energy fullerene molecular resist,” Proc. SPIE 7273, 72733D (2009).
11. J. Manyam et al., “Characterization of the base additives on a fullerene chemically amplified resist,” Proc. SPIE 7639, 76391N (2010).
12. J. Manyam et al., “Positive tone chemically amplified fullerene resist,” Proc. SPIE 8325, 83251U (2012).
13. A. Frommhold et al., “Chemically amplified fullerene resists, spin-on fullerene hardmasks and high aspect ratio etching,” in 12th IEEE Conf. Nanotechnology (IEEE-NANO), IEEE, New York (2012).
14. C. Bingel, “Cyclopolypropanation of fullerenes,” Chem. Ber. 126(8), 1957–1959 (1993).
15. X. Camps and A. Hirsch, “Efficient cyclopolypropanation of C60 starting from malonates,” J. Chem. Soc. Perkin Trans. 1, 1595–1596 (1997).
16. A. Frommhold et al., “High aspect ratio etching using a fullerene derivative spin-on-carbon hardmask,” Proc. SPIE 8328, 83280U (2012).
17. B. Paivärttana et al., “Sub-10 nm patterning using EUV interference lithography,” Nanotechnology 22(37), 375302 (2011).
18. A. Frommhold et al., “Fullerene-based spin-on-carbon hardmask,” Microelectron. Eng. 98, 552–555 (2012).
19. Y. Ekinci et al., “Evaluation of resist performance with EUV interference lithography for sub-22 nm patterning,” Proc. SPIE 8322, 83220W (2012).
20. B. Cardineau et al., “LER limitations of resist thin films,” J. Photopolym. Sci. Technol. 25(5), 633–640 (2012).
21. J. Manyam et al., “Plasma etching of high-resolution features in a fullerene molecular resist,” Proc. SPIE 7974, 79722N (2011).
22. International Technology Roadmap for Semiconductors http://www.itsr.net/Links/2012ITRS/Home2012.htm (21 6 2013)
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