Microelectronic Engineering 155 (2016) 97–101

Contents lists available at ScienceDirect

Microelectronic Engineering

journal homepage: www.elsevier.com/locate/mee

Performance of a high resolution chemically amplified electron beam resist at various beam energies

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ARTICLE INFO

Article history:
Received 8 November 2015
Received in revised form 18 February 2016
Accepted 3 March 2016
Available online 5 March 2016

Keywords:
Electron beam lithography
Molecular resist
Chemically amplification
Electron beam energy

ABSTRACT

A novel negative tone molecular resist molecule featuring a *tert*-butyloxycarbonyl protected phenol malonate group bonded to a 1,8-Diazabicycloundece-7-ene is presented. The resist shows high-resolution capability in electron beam lithography at a range of beam energies. The resist demonstrated a sensitivity of 18.7 μC/cm^2 at 20 kV. Dense features with a line width of 15 nm have been demonstrated at 30 kV, whilst a feature size of 12.5 nm was achieved for dense lines at 100 kV.

1. Introduction

As the minimum lithographic feature size in integrated circuit (IC) patterning continues to shrink, the development of both lithography tools and resist materials for the next generation of devices has become increasingly important [1,2]. With extreme ultraviolet lithography (EUVL) – considered the most promising solution for next generation lithography – delayed due to a number of technical issues as well as infrastructural immaturity [3,4], development in electron beam lithography (EBL) as an alternative for volume production has received ncreasing focus.

A number of projection electron beam and multi-beam technologies have been developed to improve throughput whilst maintaining the high-resolution capability of traditional single beam direct write systems [5,6]. Among these novel EBL technologies, several different beam energies are utilized for various application purposes. MAPPER (*MAPPER Lithography*) and other earlier microcolumn tools utilize low acceleration voltages of 5 kV or below [5,7]; A proof-of-concept multibeam mask writer from *IMS Nanofabrication* uses 50 kV electron beams [6,8]; whilst the reflective electron beam lithography (REBL) tool under development by *KLA-Tencor* uses acceleration voltages up to 100 kV [9].

With the increased demands of high volume manufacturing, high-performance electron beam resists are also required. Conventional electron beam resists generally have high resolution but poor sensitivity. Typical examples are poly(methyl methacrylate) (PMMA) and hydrogen silsesquioxane (HSQ) [10,11]. Recently, a number of advanced resist systems (mainly developed for EUVL) with good combination of sensitivity and resolution have been developed. Among them there are several high performance chemically amplified resists (CARs) such as an epoxy based negative tone molecular resist [12] and a polymer based positive tone resist [13]. Some novel non-chemically amplified resists have also been developed showing excellent resolution with reasonable sensitivity, including an organic polymer resist [14], inorganic metal-oxide nanoparticles [15] and organometallic clusters [16]. Among them the fastest electron beam resist showed a sensitivity of 2.06 μC/cm^2 (20 kV). However, its resolution was limited at 20 nm 1:2 line/space features [14]. On the other hand, the resist having the highest resolution (12 nm half pitch) requires a dose above 900 μC/cm^2 at 30 kV [15]. Although recently, particularly in extreme ultraviolet (EUV) resists, there is a trend towards non-chemically amplified resists to achieve better line edge roughness (LER) control [17], for EBL, even with multibeam technology, throughput and thus resist sensitivity is still the major limitation for application in volume production.

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http://dx.doi.org/10.1016/j.mee.2016.03.010

It is known that lithographic performance varies with different beam energies for a certain resist due to differences in energy distribution and deposition [18]. Therefore, evaluations of resist performance at various beam energies is of particular interest for newly designed resists as potential candidates for the emerging electron beam technologies.

In previous work we have developed a family of chemically amplified phenolic fullerene resists with good overall lithographic performance [19]. During the optimization and further analysis of the fullerene system, a new high performance negative tone molecular resist, xMT, has been designed [20]. The structure of the xMT molecule is shown in Fig. 1. As xMT does not contain fullerene, the cost of the material synthesis can be greatly reduced. A three-compound CAR is formulated by mixing xMT with an oligomeric epoxy crosslinker and a photo-acid generator (PAG) (Fig. 1). The reaction scheme in this resist has yet to be definitively elucidated but we propose that the xMT molecule undergoes acid catalyzed removal of the *tert*-butoxycarbonyl (*tBOC*) group, whilst the epoxy undergoes cationic ring opening. It is likely that multiple reaction pathways involving both cationic epoxy chain growth and epoxy-phenol condensation occur as shown in Fig. 2. In this study the lithographic performance of xMT resist is evaluated using EBL tools with various acceleration voltages. The durability of this resist under plasma etch is also investigated.

2. Experimental

2.1. Materials

The xMT molecule was synthesized at *Nano-C* (USA) by reacting 1,8-Diazabiccycloundecene-7-ene with *tert*-butoxycarbonyl (tBOC) protected phenol on a malonate chain. The crosslinker CL12-01, poly[(phenyl glycidyl ether)-*co*-formaldehyde] ($M_n = 1270$), was purchased from *Huntsman Advanced Materials* (USA). The crosslinker CL08–01 ($M_n = 870$), which has the same structure as CL12-01 but with a smaller molecular weight, was purchased from *Sigma Aldrich* (UK). The PAG used in this study, triphenylsulfonium hexafluoroantimonate, was purchased from *Midori Kagaku Co.* (Japan). The nucleophilic additive, triphenylsulfonium nonaflate, was purchased from *Sigma Aldrich* (UK).

2.2. Sample preparation

Resist films were spun on 18 × 18 mm silicon chips either with or without underlayer. Prior to coating of the resist or underlayer, the silicon substrates went through a simple acetone/isopropanol (IPA) clean, in which the silicon chips were ultra-sonicated for 10 min in acetone followed by another 10 min in IPA.

Resist compounds were all dissolved in ethyl lactate with a concentration of 20 g/L and blended to give a weight ratio of 0.2:2:1 for xMT, crosslinker and PAG. A nucleophilic additive is added at 5 wt% in certain cases. Spin speed is adjusted to give a resist film thickness of 30–40 nm for the sensitivity test, and 20–25 nm for high-resolution patterning. A 5-minute post-application bake (PAB) at 70 °C was applied after spin coating. After exposure, samples received a post-exposure bake (PEB) for 1 min. Samples were subsequently developed in cyclohexanone for 30 s or in *n*-butyl acetate for 1 min.

2.3. Electron beam lithography

EBL tools with various acceleration voltages were used to expose the resists. For the 20 kV and 30 kV exposures, a *FEI* XL 30 SFEG scanning electron microscope (SEM) with ELPHY Plus pattern generator (RAITH GmbH) at the University of Birmingham (UK) was used. For the 50 kV exposures, a CABL 9510C EBL system at Fundacio Institut de Ciencies Fotoniques (ICFO, Spain) was used. For the 100 kV exposures, a JBX 6300FS EBL system at the University of Leeds (UK) was used. Where possible the SEM images of resist patterns were analyzed with the software package SUMMIT to extract the LER values.

2.4. Plasma etching

Silicon etching was performed with an *Oxford Instruments* PlasmaPro NGP80 tool using inductively coupled plasma (ICP) technology. The gas mixture used was either SF_6/CHF_3 or SF_6/C_4F_8. For the SF_6/CHF_3 etch, the process conditions were 15 sccm SF_6, 50 sccm CHF_3, 20 W RF power and 200 W ICP power at 15 mT chamber pressure at 5 °C. For the SF_6/C_4F_8 etch, the conditions were 25 sccm SF_6, 30 sccm C_4F_8, 20 W RF power and 220 W ICP power. The resist thickness was measured with a surface profiler prior to etching and re-measured after silicon etching. Afterwards the residual resist was stripped with oxygen plasma and the

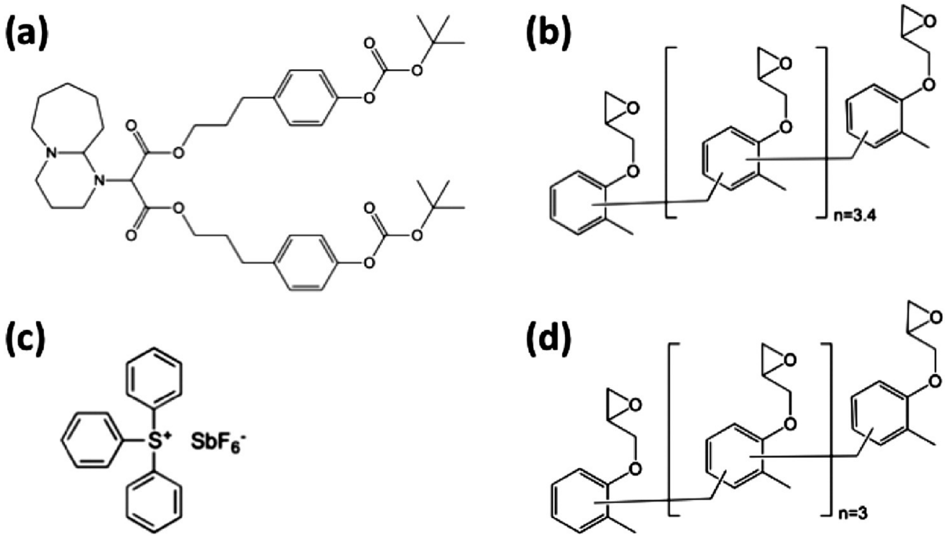

Fig. 1. Molecule structures of (a) xMT molecule, (b) epoxy crosslinker CL12-01: poly[(phenyl glycidyl ether)-*co*-formaldehyde] (Mn = 1270), (c) triphenylsulfonium hexafluoroantimonate photoacid generator, and (d) epoxy crosslinker CL08–01: poly[(phenyl glycidyl ether)-*co*-formaldehyde] (Mn = 870).

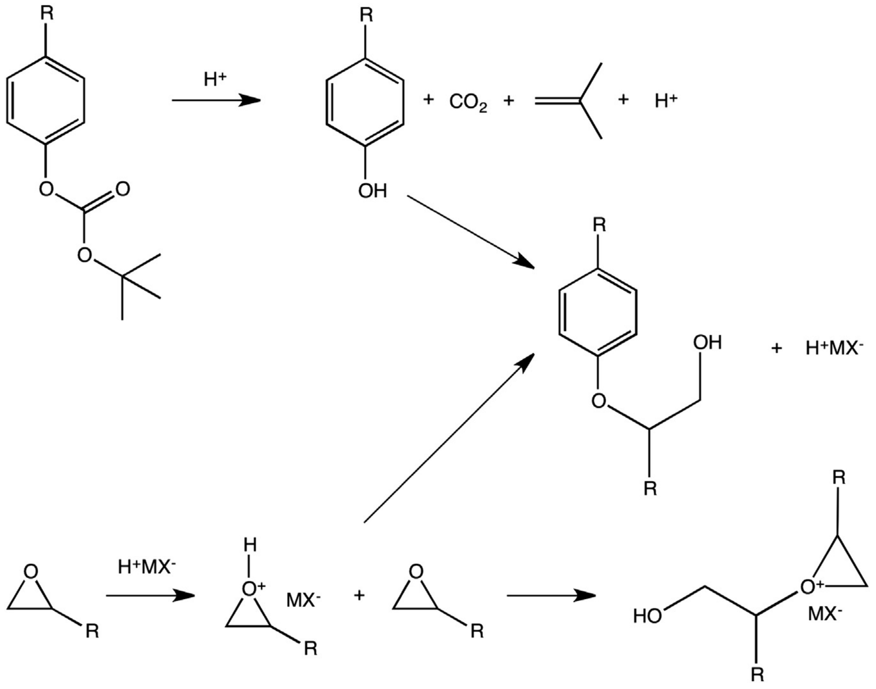

Fig. 2. Possible multiple reaction pathways in xMT resist system, including acid-catalyzed deprotection, epoxy-phenol condensation and cationic epoxy chain growth.

height of the silicon features measured again. The etch rate of the resist material was then calculated from these measurements.

3. Results and discussion

3.1. Sensitivity and pattern quality

20 kV electron beam was used to evaluate the sensitivity and contrast of xMT resist with CL12-01 crosslinker. A set of well separated, 50 × 50 μm squares was patterned with an increasing electron dose across the array. The sample was developed in cyclohexanone. A typical response curve of negative tone resists was obtained, as shown in Fig. 3(a). A sensitivity of 18.7 μC/cm^2 was observed for this resist.

To investigate the substrate compatibility and pattern quality, a set of line patterns at 50 nm pitch was patterned using a 30 kV electron beam. Various substrates were used including acetone-IPA cleaned silicon, a fullerene based carbon underlayer [21,22] and another commercial underlayer, AL412–302, from *Brewer Science*. Profile SEM images were taken by cleaving the chip across the resist lines. Fig. 3(b) shows SEM images of patterns on the three substrates. In all three samples the line profiles had steep sidewalls and no bridging between the lines, demonstrating good substrate compatibility. LER measurements reveal that using reduces the LER, especially for AL412–302 where the LER decreased from 3.8 nm to 3.1 nm. Similar results were reported in another study, that the additional organic underlayer may serve as a buffer layer to reduce the backscattering, thus improving the pattern quality [23]. The line dose for the patterns on underlayers was slightly higher than those on bare silicon, which might also due to a change in backscattering in the presence of underlayers.

As mentioned above, an additional two-step reaction scheme (deprotection and subsequent crosslinking) upon exposure is proposed and the catalytic chain length (i.e. the number of catalyzed reaction events per acid generated) might therefore decrease. As a result it is proposed that crosslinking due to acid diffusion at the interface between the exposed and unexposed areas is suppressed, providing a steep line profile and potentially high resolution.

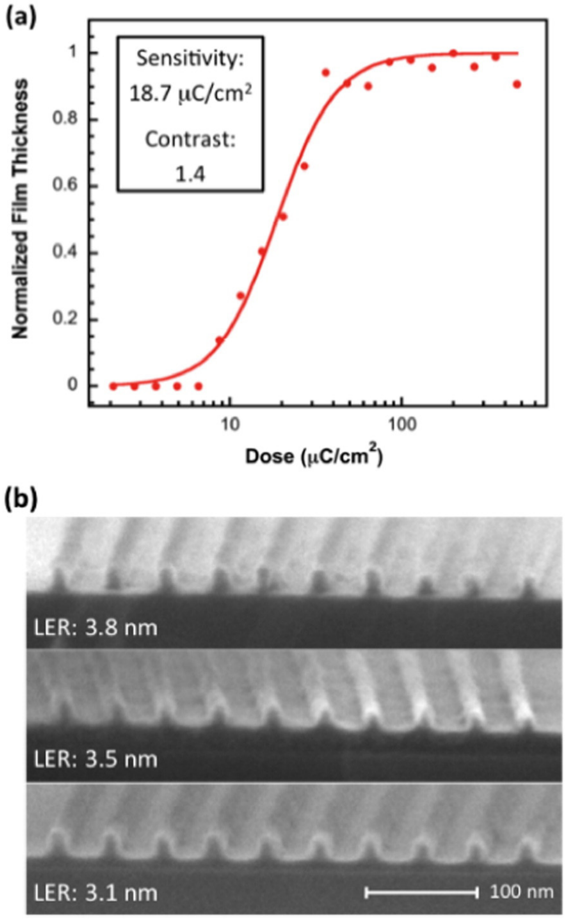

Fig. 3. (a) The response curve and measured sensitivity and contrast of xMT resist with CL12-01 crosslinker at 20 kV; (b) Profile images of 50 nm pitch lines of xMT resist on bare silicon (top), a fullerene based underlayer (middle), and a commercial underlayer, AL412–302 (bottom).

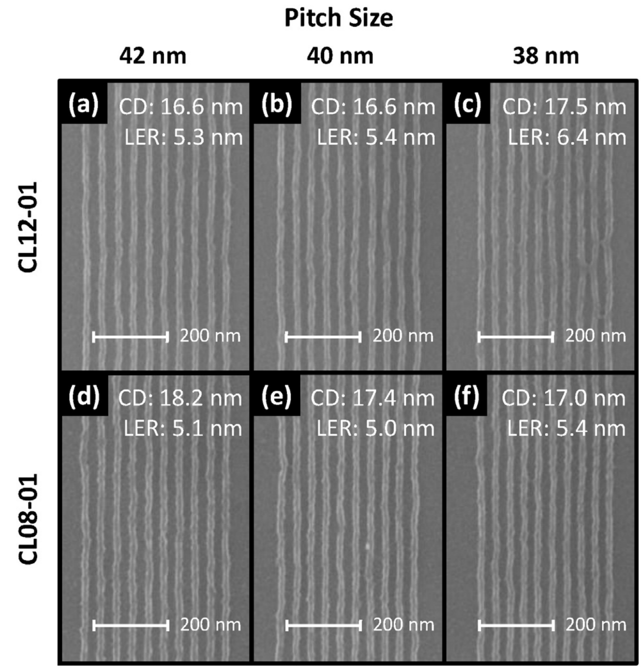

Fig. 4. The SEM images of dense features at 42 nm, 40 nm and 38 nm pitches, in xMT resist with CL12-01 (top) and CL08–01 (bottom) crosslinkers; with measured LER values. Resists were developed in cyclohexanone. The line doses are: (a) 142 pC/cm, (b) 156 pC/cm, (c) 142 pC/cm, (d) 107 pC/cm, (e) 117 pC/cm, and (f) 107 pC/cm.

3.2. Etch durability

The etch durability of the resist material was determined by performing blanket etch tests on patterned squares of xMT resist with crosslinker CL12-01 as used for the sensitivity measurements. Both SF_6/CHF_3 and SF_6/C_4F_8 mixed mode etch chemistries were investigated. As a control, Rohm and Haas SAL601, a high-durability novolac-based conventional resist, was etched under the same conditions. For SF_6/CHF_3 chemistry the resist was etched at a rate of 1.27 nm/s resulting in 7.1:1 selectivity over silicon whilst SAL601 had 1.18 nm/s etch rate with 7.8:1 selectivity. In SF_6/C_4F_8 the resist layer was etched at 1.53 nm/s with 5.5:1 selectivity in contrast to the SAL601, which was removed at a rate of 1.32 nm/s with 6.7:1 selectivity. The difference in selectivity between the two gas mixtures is caused by the higher silicon etch rate of the SF_6/CHF_3 gas mix. Comparing the results of the two materials, the xMT resist shows a slightly lower etch selectivity than the SAL601 control. In a previous study, a similar resist system with a fullerene derivative showed higher etch durability than the SAL601 [19]. The reduction in etch durability is attributed to the less aromatic nature of xMT in comparison to the fullerene derivative resulting in a higher Ohnishi number [24]

3.3. Resolution at 30 kV

With the compound ratio of [0.2:2:1] of xMT, crosslinker and PAG, the resolution capability of xMT resists with crosslinkers CL12-01 and CL08-01 were compared. The two crosslinkers have the same polymer structure but with different molecular weight. The resist sensitivities for the two crosslinkers are similar. Cyclohexanone was used as the developer. Fig. 4 shows SEM images of dense features patterned in the two formulations at various pitches.

At pitch 42 nm and 40 nm, both resists resolved with the CL08–01 sample having slightly better LER. However, at 38 nm pitch, the CL12-01 sample started showing bridging and the LER increased considerably, whilst the CL08–01 sample had no obvious bridging or collapse. This result indicates that using polymer crosslinkers with smaller molecular size can improve the resolution. This trend was also previously observed in a fullerene based molecular resist system [25]. Patterns were chosen according to the optimum LER instead of dose or critical dimension (CD). Therefore, the doses picked for the CL12-01 samples were larger due to an increased tendency to collapse at lower dose.

3.4. Resolution at various acceleration voltages

The resolution capability of xMT resists with CL08–01 crosslinker was evaluated using 30 kV, 50 kV and 100 kV electron beams. Resists were spun on acetone-IPA cleaned silicon chips. *n*-Butyl acetate was used as the developer for all samples. Dense line features were patterned and the smallest resolved pitch sizes as well as the CDs were compared. Fig. 5(a) and (b) shows SEM images of dense lines after 30 kV exposure. A minimum pitch size of 38 nm (with a 14.7 nm line width) was obtained before lines start collapsing or bridging. The line doses were 156 pC/cm and 129 pC/cm for 40 nm pitch and 38 nm pitch lines, respectively. There was also a ~1 nm LER improvement achieved compared with the cyclohexanone development.

50 kV exposure was carried out on same resist material. A slight improvement in resolution was obtained and dense features with pitch

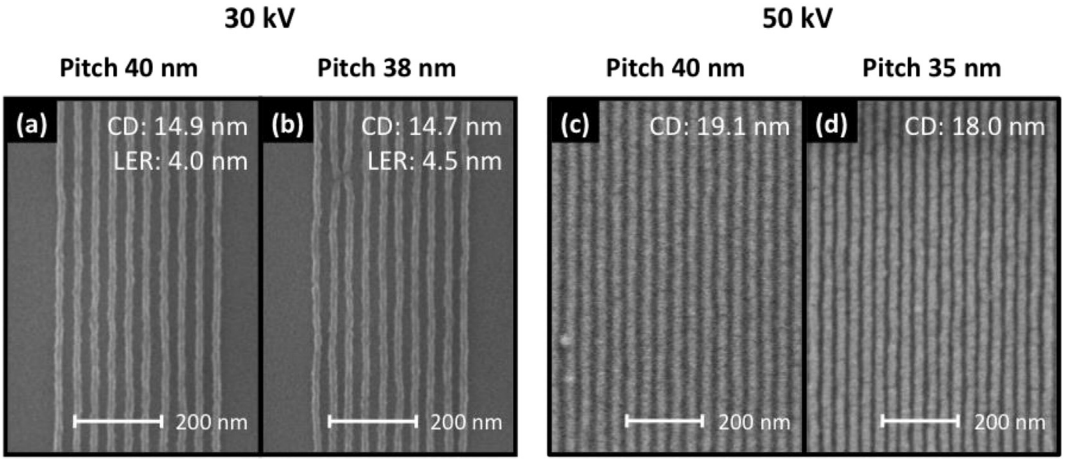

Fig. 5. (a) and (b): SEM images of xMT resist dense features at pitch 40 nm (a) and 38 nm (b), exposed with 30 kV electron beam; (c) and (d): SEM images of xMT dense features at pitch 40 nm (c) and 35 nm (d), with a ~6 nm AuPd layer sputtered on the resist patterns after development, exposed with 50 kV electron beam. The line doses are: (a) 156 pC/cm, (b) 129 pC/cm, (c) 160 pC/cm, and (d) 150 pC/cm.

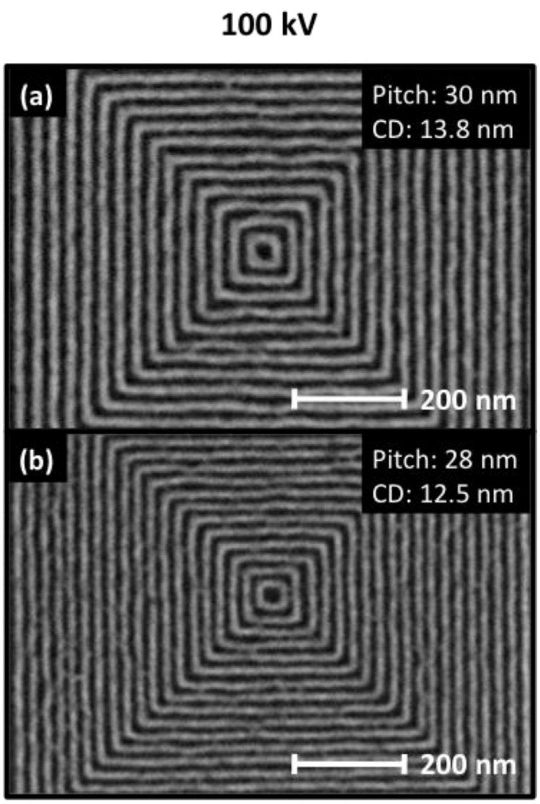

Fig. 6. The SEM images of xMT dense features at pitch 30 nm (a) and 28 nm (b), exposed with 100 kV electron beam. The line dose is 486 pC/cm for both (a) and (b).

35 nm were achieved (Fig. 5 (c) and (d)). However, the CD increased to 18 nm. Due to the imaging capability of the SEM (Inspect F50 from *FEI*) at ICFO, the samples were coated with 6 nm of AuPd through sputter coating after development but prior to imaging to improve the SEM imaging contrast. This was not required for the alternate SEM used to image the 30 kV and 100 kV samples, which has a better low contrast material capability. The additional coating might have led to an increase in line width. The line doses were 160 pC/cm for the 40 nm pitch lines and 150 pC/cm for the 35 nm pitch lines.

In the case of 100 kV exposure, significant resolution improvement was achieved. In a nested square pattern, dense features down to 28 nm pitch were successfully resolved (Fig. 6). The CD of the dense lines at 28 nm pitch was 12.5 nm. It is known that electron beam with higher acceleration voltage produces less forward scattering and backscattering, which could potentially reduce the resolution blur and proximity effect [26]. The resolution improvement at 100 kV indicates that the ultimate resolution of this resist system might be limited by the exposure tool. However, the required line dose at 100 kV was ~3 times higher than that for 30 kV electron beam, as expected [18].

4. Conclusions

A novel molecular resist material, xMT, is presented in this work. By blending this material with an oligomer epoxy crosslinker and a photoacid generator to form a negative tone chemically amplified resist, a combination of high sensitivity and high resolution was achieved. Plasma etching evaluation shows that this resist has a comparable etch resistance to the high-durability commercial electron beam resist SAL601. The lithographic performance of this resist can be further tailored by selecting the molecular size of the epoxy crosslinker. A resolution capability study of this resist at various beam acceleration voltages shows a resolution improvement with increasing beam energy, which indicates that the ultimate resolution of this resist system might still be limited by the exposure tool. In summary, this new molecular resist system has shown promising performance at various beam energies, which enables its potential applications in advanced electron beam lithography.

Acknowledgements

The authors would like to thank the Engineering and Physical Sciences Research Council (EPSRC) (EP/K503873/1) for support of this project. The authors thank Irresistible Materials Ltd. for support and provision of resist materials. The Disco DAD 321 wafer 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). D.X.Y. would like to thank Dr. Andreas Frommhold for the help and training. Also thanks to The University of Birmingham and China Scholarship Council (CSC) for support.

References

[1] International Technology Roadmap for Semiconductors, 2012 Edition, available from: http://www.itrs.net.
[2] L.R. Harriott, Proc. IEEE 89 (3) (2001) 366.
[3] U. Stamm, J. Kleinschmidt, K. Gaebel, H. Birner, I. Ahmad, D. Bolshukhin, J. Brudermann, T.D. Chinh, F. Flohrer, S. Goetze, G. Hergenhan, D. Kloepfel, V. Korobotchko, B. Mader, R. Mueller, J. Ringling, G. Schriever, C. Ziener, Proc. SPIE 5374 (2004) 133.
[4] C. Wagner, N. Harned, Nat. Photonics 4 (1) (2010) 24.
[5] T.H.P. Chang, M. Mankos, K.Y. Lee, L.P. Muray, Microelectron. Eng. 57 (2001) 117.
[6] S. Okazaki, Microelectron. Eng. 133 (2015) 23.
[7] I. Servin, N.A. Thiam, P. Pimenta-Barros, M.L. Pourteau, A.P. Mebiene, J. Jussot, J. Pradelles, P. Essomba, L. Lattard, P. Brandt, M. Wieland, Proc. SPIE 9423 (2015) 94231C.
[8] C. Klein, H. Loeschner, E. Platzgummer, Proc. SPIE 8323 (2012) 83230G.
[9] R. Freed, T. Gubiotti, J. Sun, F. Kidwingira, J. Yang, U. Ummethala, L.C. Hale, J.J. Hench, S. Kojima, W.D. Mieher, C.F. Bevis, S. Lin, W. Wang, Proc. SPIE 8323 (2012) 83230H.
[10] W.W. Hu, K. Sarveswaran, M. Lieberman, G.H. Bernstein, J. Vac. Sci. Technol. B 22 (2004) 1711.
[11] J.K. Yang, B. Cord, H. Duan, K.K. Berggren, J. Klingfus, S.W. Nam, K.B. Kim, M.J. Rooks, J. Vac. Sci. Technol. B 27 (2009) 6.
[12] R.A. Lawson, L.M. Tolbert, T.R. Younkin, C.L. Henderson, Proc. SPIE 7273 (2009) 72733E.
[13] M. Hori, T. Naruoka, H. Nakagawa, T. Fujisawa, T. Kimoto, M. Shiratani, T. Nagai, R. Ayothi, Y. Hishiro, K. Hoshiko, T. Kimura, Proc. SPIE 9422 (2015), 94220P.
[14] V. Singh, V.S.V. Satyanarayana, S.K. Sharma, S. Ghosh, K.E. Gonsalves, J. Mater. Chem. C 2 (12) (2014) 2118.
[15] J.K. Stowers, A. Telecky, M. Kocsis, B.L. Clark, D.A. Keszler, A. Grenville, C.N. Anderson, P.P. Naulleau, Proc. SPIE 7969 (2011) 796915.
[16] B. Cardineau, R.D. Re, H. Al-Mashat, M. Marnell, M. Vockenhuber, Y. Ekinci, C. Sarma, M. Neisser, D.A. Freedman, R.L. Brainard, Proc. SPIE 9051 (2014) 90511B.
[17] M. Neisser, K. Cummings, S. Valente, C. Montgomery, Y. Fan, K. Matthews, J. Chun, P.D. Ashby, Proc. SPIE 9422 (2015) 94220L.
[18] T. Takigawa, K. Kawabuchi, M. Yoshimi, Y. Kato, Microelectron. Eng. 1 (2) (1983) 121.
[19] D.X. Yang, A. Frommhold, X. Xue, R.E. Palmer, A.P.G. Robinson, J. Mater. Chem. C 2 (8) (2014) 1505.
[20] A. Frommhold, D.X. Yang, A. McClelland, J. Roth, X. Xue, M.C. Rosamond, E.H. Linfield, A.P.G. Robinson, J. Photopolym. Sci. Technol. 28 (4) (2015) 537.
[21] A. Frommhold, J. Manyam, R.E. Palmer, A.P.G. Robinson, Microelectron. Eng. 98 (2012) 552.
[22] A. Frommhold, D.X. Yang, J. Manyam, M. Manickam, E. Tarte, J.A. Preece, R.E. Palmer, A.P.G. Robinson, Nanotechnology (IEEE-NANO) 2012 12th IEEE Conference on, 2012 1.
[23] T. Kolb, C. Neuber, M. Krysak, C.K. Ober, H. Schmidt, Adv. Funct. Mater. 22 (2012) 3865.
[24] H. Gokan, S. Esho, Y. Ohnishi, J. Electrochem. Soc. 130 (1983) 143.
[25] J. Manyam, Novel resist materials for next generation lithography(PhD thesis, School of Physics and Astronomy, University of Birmingham) 2010 (Available from: http://etheses.bham.ac.uk).
[26] M.A. McCord, M.J. Rooks, in: P. Rai-Choudhury (Ed.) Handbook of microlithography, micromachining, and microfabricaiton, 1, SPIE Press, Bellingham, WA 1997, p. 157.