### PAPER

# New non-chemically amplified molecular resist design with switchable sensitivity for multilithography applications and nanopatterning

To cite this article: Neha Thakur et al 2017 J. Micromech. Microeng. 27 125010

View the article online for updates and enhancements.

## **Related content**

- <u>Phenyl-bridged polysilsesquioxane</u> <u>positive and negative resist for electron</u> <u>beam lithography</u>
  L Brigo, V Auzelyte, K A Lister et al.
- <u>Resists for sub-20-nm electron beam</u> <u>lithography with a focus on HSQ: state of</u> <u>theart</u> A E Grigorescu and C W Hagen
- <u>Study of Development Processes for ZEP-520 as a High-Resolution Positive and Negative Tone Electron Beam Lithography Resist</u> Mohammad Ali Mohammad, Kirill Koshelev, Taras Fito et al.

## **Recent citations**

- <u>A new type of sulfonium salt copolymers</u> <u>generating polymeric photoacid:</u> <u>Preparation, properties and application</u> Qiangian Wang *et al* 



# IOP ebooks<sup>™</sup>

Bringing together innovative digital publishing with leading authors from the global scientific community.

Start exploring the collection-download the first chapter of every title for free.

J. Micromech. Microeng. 27 (2017) 125010 (7pp)

# New non-chemically amplified molecular resist design with switchable sensitivity for multi-lithography applications and nanopatterning

### Neha Thakur<sup>1,3</sup>, Pulikanti Guruprasad Reddy<sup>1,3</sup>, Santu Nandi<sup>1</sup>, Midathala Yogesh<sup>1</sup>, Satinder K Sharma<sup>2</sup>, Chullikkattil P Pradeep<sup>1</sup>, Subrata Ghosh<sup>1</sup> and Kenneth E Gonsalves<sup>1</sup>

<sup>1</sup> School of Basic Sciences, Indian Institute of Technology Mandi, Kamand 175005, Himachal Pradesh, India

<sup>2</sup> School of Computing and Electrical Engineering, Indian Institute of Technology Mandi, Kamand 175005, Himachal Pradesh, India

E-mail: subrata@iitmandi.ac.in, pradeep@iitmandi.ac.in and kenneth@iitmandi.aci.in

Received 14 July 2017, revised 15 August 2017 Accepted for publication 21 August 2017 Published 7 November 2017



#### Abstract

The development of new photoresist materials for multi-lithography applications is crucial but a challenging task for semiconductor industries. During the last few decades, given the need for new resists to meet the requirements of semiconductor industries, several research groups have developed different resist materials for specific lithography applications. In this context, we have successfully synthesized a new molecular non-chemically amplified resist (n-CAR) (C3) based on the functionalization of aromatic hydroxyl core (4,4'-(9H-fluorene-9,9-diyl)diphenol) with radiation sensitive sulfonium triflates for various lithography applications. While, micron scale features have been developed using i-line (365 nm) and DUVL (254 nm) exposure tools, electron beam studies on C3 thin films enabled us to pattern 20 nm line features with L/3S (line/space) characteristics on the silicon substrate. The sensitivity and contrast were calculated from the contrast curve analysis as 280  $\mu$ C cm<sup>-2</sup> and 0.025 respectively. Being an important parameter for any newly developed resists, the line edge roughness (LER) of 30 nm (L/5S) features were calculated, using SUMMIT metrology package, to be 3.66  $\pm$  0.3 nm and found to be within the acceptable range. AFM analysis further confirmed 20 nm line width with smooth pattern wall. No deformation of patterned features was observed during AFM analysis which indicated good adhesion property between patterned resists and silicon substrates.

Keywords: molecular resist, non-chemically amplified resist, e-beam lithography, nanopatterning

S Supplementary material for this article is available online

(Some figures may appear in colour only in the online journal)

<sup>&</sup>lt;sup>3</sup>Both the authors contributed equally.

#### 1. Introduction

As a cornerstone, photolithography has been used by microelectronic industries for the manufacturing of integrated circuits (ICs) with reduced dimension [1]. Although, the critical dimensions (CD) less than 10nm node is the most challenging task in current scenario, it can be achieved by structural tuning of the resist [2-4]. In this regard, researchers have been actively involved in developing several polymeric structures which can be explored to achieve desired resolutions from higher to lower nodes [2, 5-11]. However, most of the existing polymers are reaching to their resolution limit beyond 20nm node mainly because of their large intermolecular chain entanglement, which eventually leads to the internal stress or swelling induced pattern collapse at lower nodes [2, 12–14]. To address these issues, attention has been focused on the development of molecular resists with smaller size (3-5 nm) and improved properties like monodispersity, unique dissolution behaviour and smooth thin film formations as compared to the polymers [2, 15-23]. In addition, line edge roughness (LER) is a critical parameter for higher resolution patterning applications. Because of their nanostructure dimensions, molecular resists exhibit better LER than polymers, which brings the improvement in lower node patterns below 15 nm [2, 15, 21]. Moreover, multi-layer lithography (MLL) has received greater importance for complexity of advanced devices that require alternating organic and inorganic layers for fabrication of small micro structures with high aspect ratio on a small area [24]. Ussem *et al* developed large-scale integrated organic circuits through double-layer lithography methods for pattern transfer of metal layers into the organic layer by a dry etching process [25]. Many existing resists face challenges in multilayer lithography, for example, SU-8 has a drawback as it is difficult to remove uncross-linked SU-8 from the buried locations [26]. Hence, the development of new photoresists with high-end lithography potential is highly desirable for IC industries.

It has been reported that many molecular resists have been used for unique lithography applications particularly in higher resolution patterning studies [15, 16, 22, 23]. Henderson et al developed negative tone epoxy resists for 20 nm line patterning under e-beam conditions [23]. Similarly, a few molecular resists based on calixarene and noria came into existence for higher resolution extreme ultraviolet lithography (EUVL) [15, 16, 22]. Fullerene-based resists are developed for sub-10nm line patterning applications under helium-ion beam conditions [21]. In addition, many tin, antimony, platinum, palladium and halfnium metals based inorganic hybrid photoresists have been employed for sub 20nm patterning applications with good sensitivity and resolutions [27–31]. A careful literature survey revealed that the development of resist materials with multifunctional lithographic applications is an emerging area which can be further explored for IC industries. In this regard, through functionalization of one aromatic core with sulfonium triflates, we have successfully developed an ionic molecular resist (C3) with multi-lithographic applications. To our knowledge, this is the first molecular n-CAR resist reported so far for multi-lithography applications. The resist C3 was found

to exhibit sensitivity under a range of lithographic exposure tools including i-line (UV-365 nm), deep ultra violet (DUV-254 nm) and electron beam lithography (e-beam) for micron/ nano scale patterning applications. **C3** has been successfully used for patterning 20 nm features with acceptable LER. The patterns have been characterized by SEM and AFM analysis. No deformation of patterns during AFM analysis established good adhesion between patterns and silicon substrate, which is one of the main criteria of newly developed resists for lithography applications.

#### 2. Experimental section

# 2.1. Synthesis of (4-(2-bromoethoxy)phenyl)(methyl)sulfane (C1)

**R1** (1 gm, 1.0 eq) and dry potassium carbonate (3.9 gm, 4 eq) were taken in a 100 mL round bottom flask under N<sub>2</sub> atmosphere, to this 25 mL of dry acetone was added and stirred 15 min at 0 °C. R2 (4.3 gm, 3.2 eq) was added drop wise to the reaction mixture and left stirring at 50 °C for 24h. After completion of the reaction, K<sub>2</sub>CO<sub>3</sub> was separated from the reaction mixture and the resultant filtrate was evaporated under a rotary evaporator. The pure crystalline white solid of C1 was obtained after the purification of reaction mixture through column chromatography (Eluent: Hexane). Yield: 59.6%. FT-IR:  $\nu$  max cm<sup>-1</sup> 2918, 2851 (CH), 1595, 1488, 1458 (C=C), 1422, 1382, 1274, 1238, 1212 (C-O), 1174, 1074, 1009, 852, 814, 775, 654, 571 (C-Br), 512. <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta_{\rm ppm}$  7.26 (*d*, *J* = 8.9 Hz, 2H, ArH), 6.86 (*d*, *J* = 8.2 Hz, 2H, ArH), 4.26 (*t*, *J* = 6.15 Hz, 2H, CH<sub>2</sub>), 3.62  $(t, J = 6.2 \text{ Hz}, 2\text{H}, \text{CH}_2), 2.44 (s, 3\text{H}, \text{SCH}_3); {}^{13}\text{C} \text{ NMR} (125)$ MHz, CDCl<sub>3</sub>) δ<sub>ppm</sub> 154, 148.3, 131.7, 128.3, 117.4, 95.0, 15.7. ESI-MS: *m*/*z* [M+] calcd. for C<sub>9</sub>H<sub>11</sub>BrOS: 245.971; found: 245.954; [M + 2] calculated: 247.971; found: 247.952.

#### 2.2. Synthesis of (((((9H-fluorene-9,9-diyl)bis(4,1-phenylene)) bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(4,1-phenylene)) bis(methylsulfane) (C2)

**R3** (1 gm, 1 eq) and cesium carbonate (9.12 gm, 10 eq) were taken in a 100 mL round bottomed flask under N2 atmosphere, to this 15 mL of dry dimethylformamide (DMF) was added and stirred for 15 min at 0 °C. C1 (2.42 gm, 3.5 eq) was dissolved in a 5 mL dry DMF and added drop wise to the above reaction mixture over a period of 10 min. Thereafter, the reaction mixture was left stirring at 90 °C for 5h. After completion, the reaction mixture was poured into the cold water and the organic layer was extracted with dichloromethane (DCM). The pale yellow solid was obtained after evaporation of DCM layer under rotary evaporator. Pure white solid of C2 was achieved after purification of crude reaction mixture using column chromatography (Eluent: 15% Ethyl acetate/Hexanes). Yield: 45.7%. FT-IR:  $\nu$  max cm<sup>-1</sup> 2921, 2853 (C-H), 1596, 1440, 1451 (C=C), 1373, 1240, 1219, 1178 (C-O), 1121, 1059, 929, 815, 746, 661, 610, 509, 42; <sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>)  $\delta_{\text{ppm}}$  7.75 (*d*, *J* = 7.5 Hz, 1H, ArH), 7.38-7.33 (m, 2H, ArH), 7.28-7.24 (m, 3H, ArH), 7.12 (*d*, J = 8.9 Hz, 2H, ArH), 6.86 (*d*, J = 8.25 Hz, 2H, ArH), 6.79 (*d*, J = 8.25 Hz, 2H, ArH), 4.25 (*s*, 4H, (CH<sub>2</sub>)<sub>2</sub>), 2.40 (*s*, 3H, CH<sub>3</sub>); <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>)  $\delta_{\text{ppm}}$  157.2, 157.1, 151.6, 139.9, 138.5, 129.9, 129.1, 127.6, 127.3, 125.9, 120.1, 115.3, 114.2, 66.5, 66.3, 29.6, 17.8; ESI-MS: *m/z* [M + Na] calcd. for C<sub>43</sub>H<sub>38</sub>O<sub>4</sub>S<sub>2</sub>: 705.21; found: 705.20.

#### 2.3. Synthesis of (((((9H-fluorene-9,9-diyl)bis(4,1-phenylene)) bis(oxy))bis(ethane-2,1-diyl))bis(oxy))bis(4,1-phenylene)) bis(dimethylsulfonium) trifluoromethanesulfonate (C3)

C2 (0.25 gm, 1 eq) and silver triflouoromethane sulfonate (0.24 gm, 2 eq) were taken in a 100 mL two-neck round bottomed flask under N2 atmosphere in dark conditions. To this, 15 mL of dry acetonitrile was added and stirred at room temperature for 10 min. After that, the reaction vessel was placed in an ice both at 0 °C and allowed for vigorous stirring. Methyl iodide (0.20 gm, 3 eq) was dissolved in 3 mL acetonitrile and added drop wise to the above reaction mixture over a period of 10 min and left stirring for 12 h. After completion, the white solid of silver iodide was separated from the reaction mixture and the resultant filtrate was evaporated under rotary evaporator to get a dark brown colour solid compound of C3. Yield: 42.4%. FT-IR:  $\nu$  max cm<sup>-1</sup> 3001, 2944 (C–H), 1635, 1443 (C=C), 1375, 1269 (CF<sub>3</sub>), 1158 (S=O), 1036 (C-O), 918, 750, 641, 518; <sup>1</sup>H NMR (500 MHz, DMSO-*d*<sub>6</sub>) δ<sub>ppm</sub> 7.98 (d, J = 8.9 Hz, 2H, ArH), 7.91 (d, J = 8.2 Hz, 2H, ArH), 7.40-7.37 (m, 2H, ArH), 7.32–7.27 (m, 3H, ArH), 7.02 (d, J = 8.9Hz, 2H, ArH), 6.86 (*d*, *J* = 8.95 Hz, 2H, ArH), 4.41–4.40 (m, 2H, CH<sub>2</sub>), 4.28–4.26 (m, 2H, CH<sub>2</sub>), 3.19 (s, 6H, S–(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (125 MHz, DMSO- $d_6$ )  $\delta_{ppm}$  162.4, 156.9, 151.1, 139.3, 137.9, 132.1, 128.7, 127.8, 127.5, 125.8, 121.9, 120.5, 119.4, 116.6, 116.4, 114.2, 67.1, 66.0, 63.3, 28.7; ESI-MS: m/z [M + H] calcd. for  $C_{47}H_{44}F_6O_{10}S_4$ : 1011.09; found: 1011.12.

#### 3. Results and discussions

The molecular resist ((((((9H-fluorene-9,9-diyl)bis(4,1phenylene))bis(oxy))bis(ethane-2,1-diyl))bis(oxy)) bis(4,1-phenylene))bis(dimethylsulfonium) trifluoromethanesulfonate (C3) was synthesized in a three steps synthetic approach (see figure 1). Firstly, (4-(2-bromoethoxy)phenyl) (methyl)sulfane (C1) was achieved by the reaction between 4-(methylthio)phenol (R1) and dibromoethane (R2) in dry acetone with potassium carbonate at 50 °C for 24h. Secondly, pure white solid of ((((((9H-fluorene-9,9-diyl) bis(4,1-phenylene))bis(oxy))bis(ethane-2,1-diyl))bis(oxy)) bis(4,1-phenylene))bis(methylsulfane) (C2) was synthesized by the functionalization of 4,4'-(9 H-fluorene-9,9-divl) diphenol (R3) with C1 in dry DMF using cesium carbonate as a base at 80 °C for 5 h. Finally, the brown colour solid of C3 was achieved by the reaction between C2, silvertriflouromethane sulfonate and methyl iodide at 0 °C for overnight. All synthesized materials were characterized using spectroscopic techniques than include IR, HRMS and NMR (<sup>1</sup>H, <sup>13</sup>C and <sup>19</sup>F) analysis. The detailed characterization spectra are provided in the supporting information (see figures S2-S11 (stacks.iop.org/JMM/27/125010/mmedia)).

The various structural units of C1/C2 and C3 molecules were characterized using IR and NMR spectroscopy. The absorption bands at 1000-1250, 1400-1490 and 2800- $3000 \,\mathrm{cm}^{-1}$  correspond to the characteristic C–O, C=C and -CH<sub>2</sub> stretch of the compounds C1/C2 and C3 respectively. Whereas, the absorption bands at 1158 and  $1269 \text{ cm}^{-1}$  were attributed to the S=O and CF<sub>3</sub> bond stretch of C3 (see supporting information, figures S4, S7 and S11). <sup>1</sup>H NMR signals at 6.8–7.2 ppm were due to the presence of aromatic phenyl ring in C1 molecule. Whereas, the chemical shift values observed in the case of C2 and C3 were 7.9–8.0 ppm. Methylene (-CH<sub>2</sub>-) protons of C2 and C3 were observed in the range at 4.2-4.4 ppm. Methyl protons (-CH<sub>3</sub>) on the sulfonium units of C3 were located at 3.2 ppm [11] (see supporting information, figures S2, S5 and S8). <sup>13</sup>C NMR signals observed in the range at 95-154, 114.2-157.2 and 114.29-162.42 ppm were due to the presence of various aromatic carbon atoms in C1/C2 and C3 structural units respectively. Methyl carbons in the sulfide functionality of C1 and C2 were observed at 15.7 and 17.8 ppm respectively. The chemical shift value at 28.7 ppm was due to the presence of methyl carbons on the sulfonium centre of C3 (see, supporting information, figures S3, S6 and S9). <sup>19</sup>F NMR having a peak at -77.67 ppm [11] which corresponds to the fluorine atoms (CF<sub>3</sub>) revealed the presence of triflate ( $CF_3SO_3^-$ ) functionality in C3 (see supporting information, figure S10).

After successful synthesis and characterization, we tested C3 as a new n-CAR under UV-365 and DUV-254 nm lithography tools for micron scale patterning applications. Resist solution was prepared in acetonitrile solution and spin coated with 32 nm thicknesses on the 2" p-type Si substrate at 4000 rpm speed. Prebake temperature was applied to remove excess solvent present in the thin films is 90 °C for 60 s. The surface morphology of C3 coated thin films were analysed under HR-AFM, revealed that thin films were found extremely smooth with 0.38 nm roughness (see supporting information, figure S12). A stylus profilometer was used for the thickness measurements and calculated as 32nm, which is suitable thickness for micro-/nanolithography evaluations (see supporting information, figure S13). The thin films of C3 were subjected to near-ultraviolet (UV) (365 nm) and deep ultraviolet (DUV) (254 nm) exposures for micron scale patterning applications. The post exposure bake was performed at 60 °C for 60s. Afterwards, thin films were developed with 0.02N tetramethyl ammonium hydroxide (TMAH) solution for 60s. The well-resolved micron scale features of C3 were characterized under optical microscope and revealed that C3 acts as negative tone n-CAR material under the present experimental conditions (see, figure 2). The general schematic lithographic process of C3 is shown in figure 3.

Based on the successful micron patterning studies of C3, we evaluated its nanopatterning potentials under e-beam lithography conditions. RAITH 150-Two was employed as e-beam tool for 20 nm patterning studies. Beam current and aperture used for these studies were 40.92 picoampere and 10  $\mu$ m respectively. Other lithography parameters (spinning conditions, prebake and postbake temperature, and developing condition) that were optimized during micronpatterning were



Figure 1. Chemical synthetic pathway of C3 resist.



**Figure 2.** Micron size features of C3 exposed resists thinfilms. (a) 4 and 10  $\mu$ m features patterned under UV-365 nm tool; (b) 4  $\mu$ m features patterned under DUV-254 nm tool.

kept same. Various e-beam exposure doses starting from 50-350  $\mu$ C cm<sup>-2</sup> were studied and the investigation established that 290  $\mu$ C cm<sup>-2</sup> is the minimum dose required to obtain 20 nm line patterns on the silicon substrate. The well-resolved 80-20 nm line patterns with various line/space (L/S) characteristics starting from L/10S-L/S were analysed. Figure 4 is showing different negative tone line features i.e. 20 nm (L5/S), 25 nm (L/4S), 30 nm (L/4S) and 40 nm (L/3S) obtained from the C3 resist after TMAH development. The potential to undergo minimum patterning resolution of C3 thin films under the given e-beam conditions is 20nm (L/3S) features at the dose 300  $\mu$ C cm<sup>-2</sup> (see figure 5). The higher resolution AFM images of 20 nm line features with L/5S and L/4S characteristics are shown in figure 6. C3 acts as a negative tone resist, as the exposed area remained undissolved under the present developing conditions. The detailed mechanism has been explained in the later section.

To understand the relationship between the different line features and LER, we have subjected 30, 25 and 20 nm line features of L/5S (Line/space) characteristics to 'SUMMIT' metrology analysis tool. The calculated LER parameters for 30, 25 and 20 nm (L/5S) line features are  $3.66 \pm 0.3$  nm,  $4.19 \pm 0.3$  and  $5.69 \pm 0.2$  respectively, indicate that LER is dependent on CD of the resist. The higher LER noticed for 20



**Figure 3.** An image showing general schematic lithography process of **C3** resist used for patterning of negative tone micro/nano features.

and 25 nm line features than 30 nm is mainly beacause of their poor resolution and low contrast imaging.

The sensitivity of C3 was calculated from the contrast curve. In general, contrast curve provides the information about quality of the resist [10]. Figure 7 shows the contrast curve of C3, here the relation between various e-beam



**Figure 4.** FE-SEM images of e-beam exposed C3 resist thinfilms at the dose  $300 \ \mu C \ cm^{-2}$  (a) 20 nm lines with L/5S (line/space) features; (b) 25 nm lines with L/4S (line/space) characteristics; (c) 30 nm lines with L/4S (line/space) features; (d) 40 nm lines with L/3S (line/space) characteristics.

exposure doses and their normalized remaining thickness was studied. The residual thickness of C3 patterned thin films were considered as a function of their e-beam exposure doses. Upon increasing the e-beam dose from 220–320  $\mu$ C cm<sup>-2</sup>, the thickness of C3 patterned lines were increasing gradually. This event indicated that the current resist acts as a negative tone resist. The contrast ( $\gamma$ ) and sensitivity of the resist C3 were calculated from the contrast curve and found to be 0.025 and 280  $\mu$ C cm<sup>-2</sup> respectively (see, figure 7).

Although several commercial photoresists such as NR-7, poly(methyl methacrylate) (PMMA), hydrogen silsesquioxane (HSQ) etc have been developed for the micro/nano patterning applications with fine resolutions and sensitivities, existence of new photoresists is also equally important for future lithography technologies with improved lithography potentials. The dose factors used for some of these commercial resists are very high. For example, PMMA and HSQ resists are utilized for patterning of sub-20 nm features under e-beam conditions with the dose 5.8 mC cm<sup>-2</sup> and 2000  $\mu$ C cm<sup>-2</sup> respectively [32, 33], which are found comparatively far higher than the C3 resist (280  $\mu$ C cm<sup>-2</sup>). In addition, PMMAbased resist requires organic solvent-based (ethyl acetate or MIBK: IPA) developers for the removal of exposed or unexposed regions. However, use of organic solvent as developer is generally avoided due to eco-toxicity and other health hazards [32, 34]. Similarly, NR-7 photoresists show sensitivity only toward 365 nm light. Considering all these, the present C3 resist is sensitive to wide range lithography tools (365 nm, 254 nm and e-beam) and gets developed in the presence of eco-friendly and non-toxic 0.022 N TMAH developer to pattern negative tone micro/nano features.



**Figure 5.** Magnified FE-SEM images (Mag: 58.28 KX) of 20 nm L/3S (line/space) features patterned with C3 resist at the e-beam dose  $300 \ \mu\text{C} \text{ cm}^{-2}$ .

As known from the literature, triflates are highly sensitive toward light and radiations [10, 11]. Upon irradiation with light/radiation, triflates undergo structural changes *in situ* through complex chemical transformations and generate acid products in the solid state [11]. Our recent experimental photodynamic studies established that the polar sulfonium units (Ar–S(CH<sub>3</sub>)<sub>2</sub>) get converted into non-polar sulfide (Ar–S–CH<sub>3</sub>) functionality during the lithography process [11]. These structural changes eventually led to the solubility differentiation between exposed and unexposed regions and generated negative tone patterns on the silicon substrate after development with highly polar aqueous TMAH. In addition to its negative tone patterning, as no external/additional photoacid generator



Figure 6. Top-view HR-AFM image of e-beam exposed C3 resist thinfilms: (a) 20 nm line patterns with L/5S (line/spce) characteristics; (b) 20 nm line patterns with L/4S (line/space) features.



**Figure 7.** Normalized remaining thickness (NRT) versus e-beam dose characteristics of the C3 resist for sensitivity and contrast ( $\gamma$ ) analysis.

was used to induce required polarity changes, C3 also acts as non-chemically amplified resist.

#### 4. Conclusions

In summary, we have developed a new molecular resist C3 based on the functionalization of aromatic hydroxyl core with aromatic sulfonium triflates. The synthesized resist was found to act as a potential negative tone n-CAR for various lithographic applications. The micron scale patterns were developed under UV-365 nm (i-line) and DUV-254 nm lithography tools. Most importantly, the nanoscale patterns of C3 were evaluated under e-beam conditions. Higher resolution 20 nm line patterns with L/3S (line/space) characteristics were developed with the e-beam dose 300  $\mu$ C cm<sup>-2</sup>. The sensitivity and contrast ( $\gamma$ ) of the developed C3 resist were calculated from the contrast curve as 280  $\mu$ C cm<sup>-2</sup> and 0.025 respectively. The LER of 30nm line patterns with L/5S (line/space) characteristics were calculated to be  $3.66 \pm 0.3$  nm. The AFM analyses revealed no residual resists in the developed area and the patterns are well developed. Also, no deformation of patterns during AFM studies indicated good adhesion between patterned resists and silicon substrate.

#### Acknowledgments

Financial support from the Department of Science and Technlogy (DST), India (Grant No. GITA/DST/TWN/P-69/2015) is thankfully acknowledged. AMRC, IIT Mandi is acknowledged for the infrastructural facilities. The authors acknowledge the use of the center of Excellence in Nanoelectronics (CEN) facilitates at IIT Bombay under the Indian Nanoelectronics users program (INUP), India. P G Reddy thanks to the Council of Scientific and Industrial Research (CSIR), New Delhi, India for a senior research fellowship.

#### References

- Alesso H P and Smith C F 2008 Connections: Patterns of Discovery (New York: Wiley)
- [2] Ghosh S, Pradeep C P, Sharma S K, Reddy P G, Pal S P and Gonsalves K E 2016 Recent advances in non-chemically amplified photoresists for next generation IC technology *RSC. Adv.* 6 74462–81
- [3] Mojarad N, Hojeij M, Wang L, Gobrecht K J and Ekinci Y 2015 Single-digit-resolution nanopatterning with extreme ultraviolet light for the 2.5 nm technology node and beyond *Nanoscale* 7 4031–7
- [4] Buitrago E, Fallica R, Fan D, Kulmala T S, Vockenhuber M and Ekinci Y 2016 SnO<sub>x</sub> high-efficiency EUV interference lithography gratings towards the ultimate resolution in photolithography *Microelectron. Eng.* 155 44–9
- [5] Lawrie K J, Blakey I, Blinco J P, Cheng H H, Gronheid R, Jack K S, Pollentier I, Leeson M J, Younkin T R and Whittaker A K 2011 Chain scission resists for extreme ultraviolet lithography based on high performance polysulfone-containing polymers *J. Mater. Chem.* 21 5629–37
- [6] Tejero V C, Carrasco S, Villoslada F N, Fierro J L G, Sanchez M C C C, Bondi M C M and Barrios C A 2013 Ultrasensitive non-chemically amplified low-contrast negative electron beam lithography resist with dual-tone behaviour J. Mater. Chem. C 1 1392–8
- [7] Moon S and Kim J M 2007 Chemistry of photolithographic imaging materials based on the chemical amplification concept J. Photochem. Photobiol. C 8 157–73
- [8] Sanders D P 2010 Advances in patterning materials for 193 nm immersion lithography *Chem. Rev.* 110 321–60
- [9] Okoroanyanwu U, Byers J, Shimokawa T and Willson C G 1998 Alicyclic polymers for 193 nm resist applications: lithographic evaluation *Chem. Mater.* 10 3328–33

- [10] Reddy P G, Pal S P, Kumar P, Pradeep C P, Ghosh S, Sharma S K and Gonsalves K E 2017 Polyarylenesulfonium salt as a novel and versatile nonchemically amplified negative tone photoresist for high-resolution extreme ultraviolet lithography applications ACS Appl. Mater. Interfaces 9 17–21
- [11] Satyanarayana V S V, Kessler F, Singh V, Scheffer F R, Weibel D E, Ghosh S and Gonsalves K E 2014 Radiationsensitive novel polymeric resist materials: iterative synthesis and their EUV fragmentation studies ACS Appl. Mater. Interfaces 6 4223–32
- [12] Thackeray J W 2011 Materials challenges for sub-20 nm lithography J. Micro/Nanolithogr. MEMS MOEMS 10 033009
- [13] Naulleau P P et al 2011 Critical challenges for EUV resist materials Proc. SPIE 7972 797202
- [14] Yayi W, Markus B, Wolf-Dieter D, Antje L and Michael S 2007 Performance of chemically amplified resists at Halfpitch of 45 nm and bellow *Proc. SPIE* 65190R
- [15] Solak H H, Ekinci Y, Käser P and Park S 2007 Photon-beam lithography reaches 12.5 nm half-pitch resolution *J. Vac. Sci. Technol.* B 25 91–5
- [16] Fujita J, Ohnishi Y, Ochiai Y and Matsui S 1996 Ultrahigh resolution of calixarene negative resist in electron beam lithography Appl. Phys. Lett. 68 1297–9
- [17] Lawson R A, Tolbert L M and Henderson C L 2010 High sensitivity nonchemically amplified molecular resists based on photosensitive dissolution inhibitors *J.Vac. Sci. Technol.* B 28 C6S12–8
- [18] Nishikubo T and Kudo H 2011 Recent development in molecular resists for extream ultraviolet lithography *J. Polym. Sci. Technol.* 24 9–18
- [19] Dai J, Chang S W, Hamad A, Yang D, Felix N and Ober C K 2006 Molecular glass resists for high-resolution patterning *Chem. Mater.* 18 3404–11
- [20] Robinson A P G, Palmer R E, Tada T, Kanayama T and Preece J A 1998 A Fullerene derivative as an electron beam resist for nanolithography *Appl. Phys. Lett.* 72 1302–4
- [21] Shi X, Prewett P, Huq E, Bagnall D M, Robinson A P G and Boden S A 2016 Helium ion beam lithography on fullerene molecular resists for sub-10 nm patterning *Microelectron*. *Eng.* 155 74–8
- [22] Niina N, Kudo H, Oizumi H, Itani T and Nishikubo T 2013 Synthesis and property of noria (water-wheel like macrocycle) derivatives with pendant alkoxyl and adamantyl ester groups, and their application for extreme ultraviolet resist *Thin Solid Films* 534 459–64

- [23] Lawson R A, Lee C T, Tolbert L M, Younkin T R and Henderson C L 2009 High resolution negative tone molecular resist based on di-functional epoxide polymerization *Microelectron. Eng.* 86 734–7
- [24] Shih W S, Neef C J and Daffron M G 2004 A planarization process for multi-layer lithography applications *Proc. SPIE* 5376 664–72
- [25] Liu S, Shadeedi A A, Kaphle V, Keum C M and Ussem B L 2017 Patterning organic transistors by dry-etching: the double layer lithography Org. Electron. 45 124–30
- [26] Chiriacò M S, Bianco M, Amato F, Primiceri E, Ferrara F, Arima V and Maruccio G 2016 Fabrication of interconnected multilevel channels in a monolithic SU-8 structure using a LOR sacrificial layer *Microelectron. Eng.* 164 30–5
- [27] Re R D, Passarelli J, Sortland M, Cardineau B, Ekinci Y, Buitrago E, Neisser M, Freedman D A and Brainard R L 2015 Low-line edge roughness extreme ultraviolet photoresists of organotin carboxylates J. Micro/Nanolithogr: MEMS MOEMS 14 043506
- [28] Sortland M, Hotalen J, Re R D, Passarelli J, Murphy M, Kulmala T S, Ekinci Y, Neisser M, Freedman D A and Brainard R L 2015 Platinum and palladium oxalates: positive-tone extreme ultraviolet resists J. Micro/ Nanolithogr. MEMS MOEMS 14 043511
- [29] Passarelli J, Murphy M, Re R D, Sortland M, Dousharm L, Vockenhuber M, Ekinci Y, Neisser M, Freedman D A and Brainard R L 2015 High-sensitivity molecular organometallic resist for EUV (MORE) *Proc. SPIE* 9425 94250T
- [30] Bae W J, Trikeriotis M, Sha J, Schwartz E L, Rodriguez R, Zimmerman P, Giannelis E P and Ober C K 2010
  High refractive index and high transparency HfO2
  nanocomposites for next generation lithography J. Mater. Chem. 20 5186–9
- [31] Kasahara K, Xu H, Kosma V, Odent J, Giannelis E P and Ober C K 2017 Nanoparticle photoresist studies for EUV lithography *Proc. SPIE* 10143 1014308
- [32] Duan H, Winston D, Yang J K W, Cord B M, Manfrinato V R and Berggren K K 2010 Sub-10 nm half-pitch electronbeam lithography by using poly (methyl methacrylate) as a negative resist J. Vac. Sci. Technol. B 28 C6C58
- [33] Gangnaik A S, Georgiev Y M and Holmes J D 2017 New generation electron beam resists: a review *Chem. Mater.* 29 1898–917
- [34] Carbaugh D J, Wright J T and Rahman F 2017 Negative tone photolithography with photo-sensitised polymethyl methacrylate (PMMA) *Microelectron. Eng.* 171 53–9