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Satinder K. Sharma, Manvendra Chauhan, Rudra Kumar, Kumar Palit, Sumit Choudhary, Kenneth E. Gonsalves, "Development of metal-organic cluster based negative tone resist: pre-screened through the helium-ion beam prelude to extreme ultraviolet lithography (EUVL) applications," Proc. SPIE 11612, Advances in Patterning Materials and Processes XXXVIII, 1161208 (22 February 2021); doi: 10.1117/12.2583850

Event: SPIE Advanced Lithography, 2021, Online Only

Development of Metal-Organic Cluster based Negative Tone Resist: Pre-screened through the Helium-ion Beam prelude to Extreme Ultraviolet Lithography (EUVL) Applications

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ABSTRACT

EUV lithography (EUVL) is expected to offer a single-exposure solution down to 5 nm or below nodes. To successfully implement EUVL for sub-10 nm nodes on time, one major hurdle is the availability of compatible resists with sufficiently low line edge/width roughness (LER/LWR) and low exposure dose. Hence, the requirements of high-resolution patterning along with sub 10 nm feature size necessitates nanocluster size resist materials with high irradiation absorption coefficients, considerably high sensitivity, and permissible LER and LWR. To meet the aforementioned requirements, we formulated a negative tone metal-core (indium and copper) organic clusters resists such as In-MOCs and Cu-MOCs having a nanosize domain. In-MOCs is comprised of indium core as an inorganic metal building unit and methacrylic acid (MAA) as an organic ligand while the Cu-MOCs is comprised of copper metal core and trans 2,3 dimethylacrylic acid (DMA) organic ligand through the versatile sol-gel method. The incorporation of indium and copper metal provides the enhanced absorption of irradiation beams, while the MAA and DMA in the formulated resist showing radical polymerization could be easily crosslinked through the carbon-carbon bond with the minimal amount of exposure dose of He^+ ions to form a negative tone resist. The designed resists exhibit a significantly higher sensitivity of ~12.76 μC/cm^2 and ~14.93 μC/cm^2 towards the helium ion beam for In-MOCs and Cu-DMA resists, respectively. The well-resolved half-pitch features of ~13 nm and the minimum line width of ~11 nm L/2S with the substantial helium-ion dose of ~30 μC/cm^2 for In-MOCs resist, whereas, the well-resolved high resolution (HR) ~ 10 nm half-pitch (HP) and ~9 nm (L/2S) line patterns at a considerable He^+ dose of ~35 μC/cm^2 for Cu-DMA resist. The calculated LER and LWR for 13 nm half-pitch patterns are 2.56 ± 0.06 nm and 2.48 ± 0.08 nm, respectively for In-MOCs resist, while the computed line edge roughness (LER), line width roughness (LWR) for HR~10 nm (HP) line patterns are 2.24 ± 0.08 nm and 3.1 ± 0.09 nm, respectively for Cu-DMA resist.

Keywords: Indium metal-organic cluster, Copper metal-organic cluster, Helium ion beam lithography, sub 10 nm resolution, Line edge/width roughness, EUV lithography

1. INTRODUCTION

EUV lithography (EUVL) is considered to be one of most promising technology for sub 10 nm, HP node of semiconductor manufacturing. In order to support new technology an outspread array of new resists have been introduced. However, to eliminate the resist material showstoppers, EUV resists simultaneous need to meet the resolution, linewidth roughness and sensitivity (RLS) patterning requirements laid out in the International Technology Roadmap for semiconductor to support process development. [1, 2] Additionally, Electron beam lithography (EBL) is also the most versatile lithography prototyping tool for sub 10 nm nodes or below

Advances in Patterning Materials and Processes XXXVIII, edited by Daniel P. Sanders, Douglas Guerrero, Proc. of SPIE Vol. 11612, 1161208 · © 2021 SPIE
CCC code: 0277-786X/21/$21 · doi: 10.1117/12.2583850

patterning.[3, 4] Apart from EBL, helium ion beam lithography (HIBL) is recently introduced & utilized as a potential lithography tool due to its low backscattered ions in face of EBL, low proximity effect, small lateral scattering, and small beam spot size.[5-7]

On top of novel lithographic techniques to realize the aforementioned requirements, designing of new resist materials are essential to meet the new technology nodes and can address the issues of the patterning challenges facing in the current lithography industry. Traditional, chemically amplified resists (CARs) along with the respective photoacid generator (PAG) content have been widely incorporated owing to improved resolution on the cost of significant sensitivity reduction ,which hinders the practical applications of sub 10 nm technology nodes or below.[8]

In the light of increase absorption of EUV photons, in the recent past a metal-based resist material have been seriously examined and also a noteworthy effort to try to alleviate industry understanding towards the integration of metal resists onto next generation fab-friendly processes, unduly undertaken. Explicitly, hybrid resist such as nano particles based resists, and metal-organic clusters-based (MOC_s) resist have been recently adapted as an evolving candidate due to high-resolution features, higher sensitivity, and high etch resistance.[9-13] Higher etch resistance of hybrid resist materials, eliminate the pattern collapse during the pattern transfer process. Various metal-oxide based resists such as zirconium, hafnium, and zinc oxide have been studies using EBL with high-resolution line patterns and minimal doses. Furthermore, the MOCs based resist can also be used with and without the addition of any additives. Recently, our group successfully demonstrated the formulation of the hybrid resist comprising Ag NPs incorporated TER-polymer resist which shows the dual-tone behaviour using EBL/HIBL.[14] Also, a Ni-MOCs based resist was also developed through the sol-gel method for high resolution sub-10 nm line patterning as a negative tone resist using EBL/HIBL.[13]

In order to meet the next generation technology node challenges, the hybrid resists might be possible alternate to enables the high resolution pattering of 10 nm or below with desired RLS. In this context, herein, we designed and developed an inorganic-organic based copper metal-organic cluster and indium metal-organic cluster resists formulations for high resolution patterning. The former is formulated using copper (Cu) core and ligand trans-2,3 dimethyl acrylic acid (DMA) and later is synthesized using indium metal as metal core and methacrylic acid (MAA) as ligand through sol-gel synthesis. Indium and copper metals show high absorption crossection towards extreme ultraviolet lithography (EUVL) and high optical density with respect to carbon (O.D= 10-12) wherein each incoming EUV photons, EBL electrons and HIBL ions cause multiple chemical reactions within the resists formulation, significantly improving sensitivity and resolution. The developed resists could form a uniform thin film and shows well-developed negative tone resist with sub-10 nm feature, low LER/LWR in HIBL. Our developed resists In-MAA, as well as Cu-DMA, can be further used as a potential candidate for EUVL dense and complex patterning.

The lithographic performances of In-MAA and Cu-DMA, MCOC resists using He^+ beam lithography system are discussed in the following sections. Additionally, the contrast-sensitivity curve, as well as etch resistance of the newly developed, resists have also been investigated and demonstrated in this study.

2. EXPERIMENTAL SECTION

2.1 Materials: Indium (III) acetate hydrate, copper (II) acetate monohydrate, methacrylic acid, *trans*-2,3-dimethylacrylic acid were purchased from Aldrich. Ethyl acetate, triethyl amine and ethyl lactate was purchased from TCI chemicals.

2.2 Synthesis of resists

In-MAA and Cu- DMA resists, both were synthesized by the sol-gel method. Copper metal salt was mixed with ethyl acetate to form homogenous solution A. Likewise, trans-2,3-dimethylacrylic acid, trimethylamine, and ethyl acetate were mixed to form solution B. Thereafter, the solution B was gently poured into solution A dropwise at 70 °C with continuous stirring. The reaction was carried out at 70 °C for 24 hours and the final product was subsequently and repeatedly washed with toluene and dried in an oven at 50 °C for 4 hours. The synthesized Cu-DMA resist was then stored in a vacuum desiccator. In-MAA resist was synthesised using a similar procedure in which DMA was replaced with MAA.

2.3 Thin film preparation

3 wt. % of the synthesized resists and 1 wt. % Bis(4-*tert*-butylphenyl)iodonium triflate was dissolved in ethyl lactate solution with the aid of vortex mixture. Then the solution was filtered through 0.22 um pore sized membrane via a syringe filter to remove the unwanted micron size particles. After that, the solution was spin-coated at 3000 rpm for 45 sec on RCA cleaned silicon wafer to form a thin film. The coated resist films was prebaked at 90^{o}C for 45 sec.

2.4 Helium ion Beam Lithography (He^+BL)

He^+BL (Zeiss ORION Nano Fab system) was performed with 30 KV, He^+ beam on ~30 nm thin resists film at the current ~ 0.25 pA using ~10 µm numerical aperture. After being exposed with He^+ beam, negative tone patterns were developed in propane-1-ol : Propionic acid mixture where the exposed thin films were dipped for 1 min 30 sec.

2.5 Characterization

Field emission scanning electron microscopy (FESEM, Zeiss, Gemini SEM 500, Germany) was used to analyse the surface morphology of the nano-patterns. Reactive ion etching (RIE) was performed over MCOC resists films using the Planar Tech RIE instrument, atomic force microscope (AFM) (Bruker Icon) was used to analyse the film thickness and surface morphology. The LER and LWR parameters for exposed line-patterns were measured by industry-standardized metrology software SuMMIT®.

3. RESULTS AND DISCUSSION.

3.1 High-resolution patterning of MCOC resists

To examine the patterning capability of newly formulated MCOC resists, Cu-DMA and In-MAA, both were exposed under He^+ beam. The film thickness for both MCOC resists was kept the same as ~30 nm. The exposure parameters and patterns matrix were also kept the same for both resists. The presence of metal core in the resists increases the etch resistance, which will be discussed later on in the section for etch resistance analysis and have also played a role to increase the sensitivity of both resists formulations, whereas the ligands such as DMA and MAA attached to the metal core are weaker binding ligand, thus instigate the ligand exchange mechanism at a lower exposure dose and gave negative tone patterns.[15] After analyzing the negative tone high resolution features patterned on Cu-DMA and In-MAA, MCOC resists using FESEM tool, we found that the Cu-DMA resists can produce up to minimum ~ 10 nm hp (i.e. ~10 nm L/S features) and 9 nm critical dimension (CD) with the L/2S features, whereas ~13 nm, HP and CD of 11 nm L/2S were well resolved with In-MAA resists. Figure 1, showed the Cu-DMA patterns of line-width 15 nm and 10 nm with L/S features and 9 nm L/2S features at the He^+ beam dose of ~35 µC/cm^2. The computed LER and LWR for the 10 nm, hp lines patterned on Cu-DMA resist are 2.24 ± 0.08 nm and 3.1 ± 0.09 nm, respectively. Figure 2 showed the well-developed high-resolution patterns of In-MAA resists of line-width ~ 15 nm and ~13 nm with L/S features and critical dimension (CD) of 11 nm L/2S at the He+ beam dose of ~30 µC/cm2. The computed LER and LWR for the 13 nm, hp lines patterned on In-MAA resist are 2.56 ± 0.06 nm and 2.48 ± 0.08 nm, respectively.

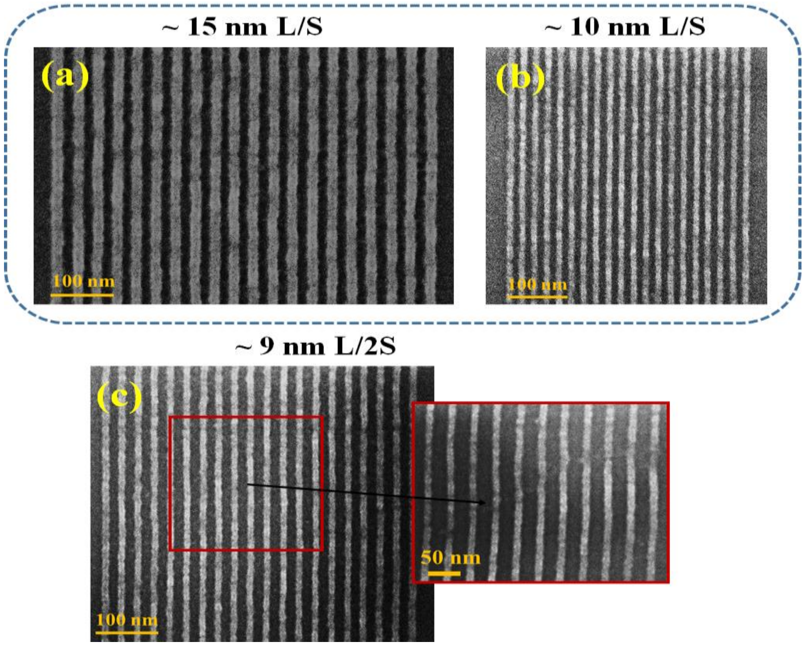

Figure 1. FESEM images of exposed Cu-DMA MCOC resist, using He+ beam (a) 15 nm L/S (b) 10 nm L/S and (c) 9 nm L/2S at the dose 35 μC/cm2.

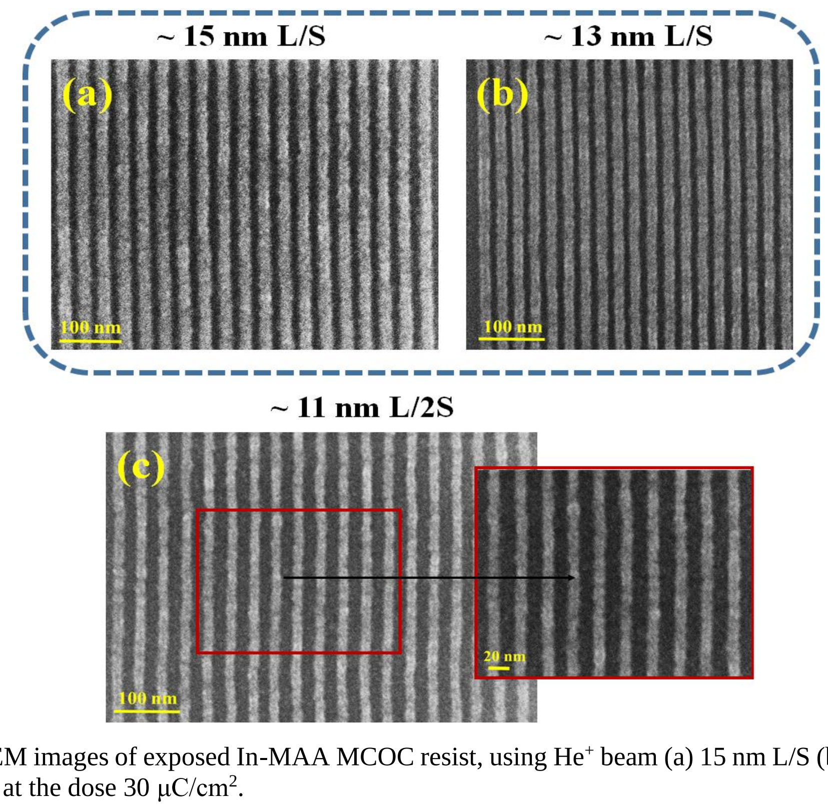

Figure 2. FESEM images of exposed In-MAA MCOC resist, using He^+ beam (a) 15 nm L/S (b) 13 nm L/S and (c) 11 nm L/2S at the dose 30 $\mu C/cm^2$.

In order to further illustrate the surface morphology of He^{+} beam exposed and well-developed high-resolution patterns of both MCOC resists, the AFM micrographs of 15 nm L/5S patterns of Cu-DMA and In-MAA are exhibited in Figure 3 (a) and (b), respectively. It can be clearly observed that the patterns were well resolved after development and left no residue behind. After the development of both ~ 30 nm exposed MCOC resists films, the measured height of the well-developed patterns was around ~25 nm and ~22 nm for Cu-DMA and In-MAA MCOC resists, respectively. This indicates that the developer and the development process used for both the resists is perfectly optimized.

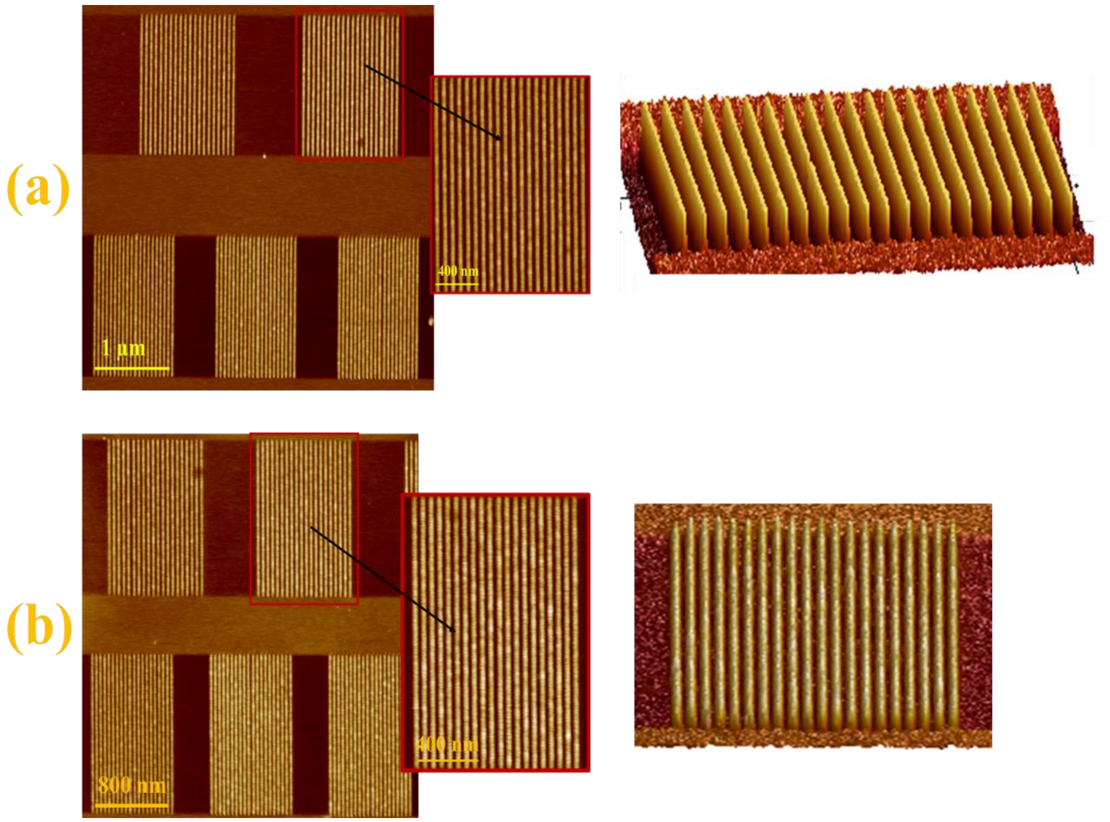

Figure 3. AFM images of 15 nm L/5S line features of (a) Cu-DMA, and (b) In-MAA MCOC resists

With aim to examine the sensitivity and contrast for both the newly developed MCOC resists, Cu-DMA and In-MAA, we exposed the normalized remaining thickness (NRT) analysis patterns of area 500 nm^2 on both the resists under 30 KV, He^{+} beam at the dose ranging from 2 $\mu C/cm^2$ to 100 $\mu C/cm^2$ with the step of 2 $\mu C/cm^2$. The contrast curves for both the resists are presented in Figure 4.

In the case of Cu-DMA, the dose required to print 500 nm^2 patterns i.e. sensitivity ($E_{Cu\text{-}DMA}$) is 14.93 $\mu C/cm^2$ and contrast ($\gamma_{Cu\text{-}DMA}$) is 1.025, whereas, the sensitivity ($E_{In\text{-}MAA}$) and contrast ($\gamma_{In\text{-}MAA}$) for In-MAA were calculated as 12.76 $\mu C/cm^2$ and 0.982, respectively. However, the high resolution (HR) well resolved sub-15 nm line features were patterned at 35 $\mu C/cm^2$ and 30 $\mu C/cm^2$ on Cu-DMA and In-MAA resists, respectively. Moreover, sensitivity calculated for In-MAA and Cu-DMA resists were noticed better than our previous work on Ni-DMA MCOC resist.[16]

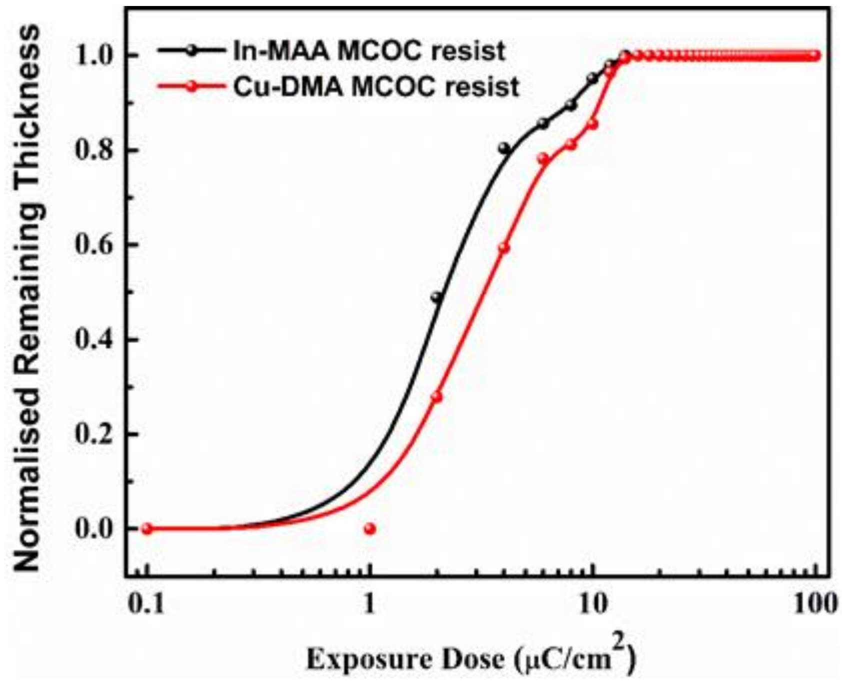

Figure 4. Normalized remaining thickness vs He^{+} beam doses characteristics for Cu-DMA and In-MAA MCOC resists.

3.2 Etch resistance analysis for MCOC resists

To present our newly developed highly sensitive Cu-DMA and In-MAA MCOC resists as the potential resists to high volume manufacturing (HVM) of next-generation silicon technology, the establishment of etch resistance of the resists with respect to the silicon is exceedingly desirable. Hence, in this section, we compared the etch rate of the Cu-DMA and In-MAA resists with the silicon wafer.

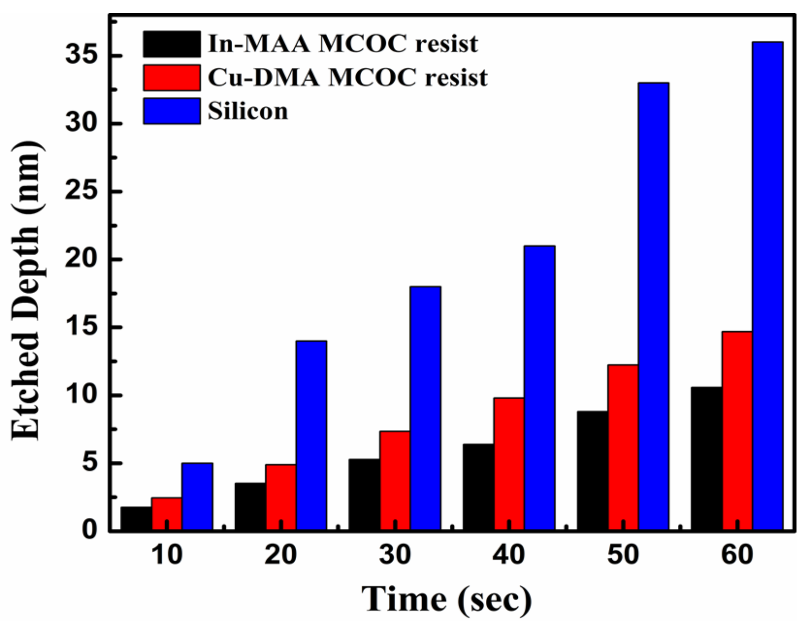

Figure 5. Etched depth comparison with respect to the time for the Cu-DMA, In-MAA MCOC resists and silicon wafer.

For this experiment, SF_6 was used as an etching precursor at the rate of 25 sccm with 1.5 mTorr pressure. RF power of 60 Watt was used during the experiment. The etch rates were evaluated by measuring the depth profile etched on both the MCOC resists and silicon samples using atomic force microscopy (AFM), analysis.

The calculated etch rates of Cu-DMA, In-MAA, and silicon wafers were 0.244 nm/sec, 0.176 nm/sec, and 0.6 nm/sec, respectively. These etch rates provides the fact that the In-MAA resists exhibit 1.38 times lower etch rate, obviously higher etch resistance in comparison to the Cu-DMA resists. Figure 5 showed the comparisons for the etched depth profile for Cu-DMA and In-MAA MCOC resists with the silicon wafers at successive time intervals of 10 sec, 20 sec, 30 sec, 40 sec, 50 sec, and 60 sec.

4. CONCLUSIONS

In conclusion, we formulated two novel metal-organic cluster resists formulations that utilize high optical density copper (Cu- OD 10 w.r.t Carbon) and indium (In O.D = 12 w.r.t. Carbon) metal node which possesses high irradiation absorption cross-section, and DMA and MAA as organic ligands to crosslink the molecules with the minimal He^+ doses ~35 $\mu C/cm^2$, and 30 $\mu C/cm^2$, respectively. Both of these newly designed MCOC resists exhibit considerably lower etch rates w.r.t the silicon i.e. Cu-DMA etched 2.4 times slower than Silicon whereas In-MAA etched with the rate 3.4 times slower than the silicon at the same recipe. These results indicate the exceptional lithographic performances and benefits of high sensitivity towards He^+ beam, high etch resistance of both MCOC resists w.r.t the silicon established these resists formulations as the potential candidates for the next generation lithography applications.

ACKNOWLEDGMENT

Authors thank the Department of Science and Technology (DST) and Technology Systems Development Program (TSDP), India for financial support through sanctioned project reference number: DST/TSG/AMT/2015/634. Rudra Kumar thanks the Science and Engineering Research Board (SERB) New Delhi, India for the national postdoc fellowship (Sanction Project reference number: PDF/2017/001437). The authors also acknowledge the Centre for Design and Fabrication of Electronic Devices (C4DFED); Class 100 cleanroom facility, Indian Institute of Technology (IIT), Mandi, MANDI (Himachal Pradesh), India for use of various sample preparation and state of art Zeiss Orion NanoFab, HIBL, and Raith e-Line PLUS, EBL patterning facilities for lithography and Zeiss, Gemini SEM 500, FESEM for imaging work available at C4DFED facility at IIT Mandi, India.

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