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All New Nickel Based Metal Core Organic Cluster (MCOC) Resist for N7+ Node Patterning

Satinder K. Sharma[1*], Rudra Kumar[1], Manvendra Chauhan[1], Mohamad G. Moinuddin[1], Jerome Peter[1], Subrata Ghosh[2], Chullikkattil P. Pradeep[2], and Kenneth E. Gonsalves[2**]
*****satinder@iitmandi.ac.in[1]; **kenneth@iitmandi.ac.in[2]***

[1]School of Computing and Electrical Engineering (*SCEE*), Indian Institute of Technology (IIT)-Mandi, Mandi -175005 (Himachal Pradesh), India.
[2]School of Basic Science (*SBS*), Indian Institute of Technology (IIT)-Mandi, Mandi -175005 (Himachal Pradesh), India.

Abstract

The increase in the demand of sub-10 nm feature size in semiconductor industries necessitates a new kind of resist material development which can absorb a large fraction of irradiaion and retains the small size cluster distribution (1-2 nm). In this context, we developed a novel nickel-based organo-metallic cluster comprising high optical density inorganic nickel as metal building units (MBU), and 3,3-Dimethylacrylic acid as an organic ligand to form Ni-DMA clusters. The synthesised clusters have ~1 nm size with narrow size distribution. The formulated resist shows the negative tone pattern when exposed with a focused helium ion (He^+) beam and e-beam. The high-resolution line patterns of ~8 nm at the dose of ~40 μC cm^{-2} were obtained with the minimum line edge roughness (LER) and line width roughness (LWR) of 2.16 ± 0.04 nm and 3.03 ± 0.06 nm, respectively.

Keywords: Metal core organic cluster, helium ion beam lithography, sub–10 nm node, negative tone resist, semiconductor processing.

1. INTRODUCTION

To keep alive the current semiconductor industry, it demands rapid development in the key forces responsible for this growth. Since 1965, device pitch has been decreasing half every 18 months or less according to celebrated Moore's law.[1,2] Presently, as we approached its physical and device physics limits, it is essentially required to adopt new process technology and materials which are out of this beaten track. To push the device dimension down to 7 nm (N7+ node)[3], it is also required to investigate its skeleton to be at the same limit in particularly, photoresist. In the development of photoresist materials, it is essentially requirement of the resist formulation with low molecular weight and high optical density. Low molecular weight (M_w) clusters with metal core provide good agreement in LSR *(LER-Sensitivity-Resolution*) trade-off. It is also beneficial to develop metal core organic cluster (MCOC) that can absorb high fluence of incident irradiation, and must retain small cluster diameter (1-2 nm).[4,14] Apart from the metal, the sensitivity also differentiates with the type of ligand used in the formulation of the metal-core resists.[5] Chakrabarty et al,[6] have also investigated the dissolution rate and sensitivity by altering the core-ligand interaction and found the DMA ligand better than methacrylic acid due to its soft bonding with the metal-core.

In this context, we developed a novel nickel (Ni) based MCOC resists comprising high optical density inorganic nickel as metal building units (MBU), and 3,3-Dimethylacrylic acid (DMA) as an organic ligand to form Ni-DMA clusters. The synthesized clusters have homogeneous ~1 nm size distribution. The formulated resist shows negative tone patterns when exposed with a focused He^+ beam and e-beam. It was also observed that synthesized MCOC has second-order photon interaction, where incident irradiation has been transferred to the nearby organic cluster through Ni and hence enhanced the sensitivity as compared to other metal-based resists.[7] This inorganic-organic hybrid nature of synthesized resist provides high etch resistance for the standard Si pattern transfer process. Consequently, the high resolution below ~10 nm, advanced patterning with trivial proximity effect of Ni-DMA resist formulation support, it's candidature with standard semiconductor processing conditions at N7+ technology node of the electronic industry.

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

2. EXPERIMENTAL SECTION.

Materials: Nickel acetylacetonate, 3,3-Dimethylacrylic acid were purchased from Aldrich. Ethyl acetate, triethyl amine, methyl isobutyl ketone (MIBK), and isopropanol (IPA) were purchased from S D fine chemicals (SDFCL). Ethyl lactate was purchased from TCI chemicals.

2.1 Synthesis of Nickel-3,3-Dimethylacrylic acid (Ni-DMA) resist

Ni- DMA resists materials were synthesized by the sol-gel method. Nickel acetylacetonate was mixed with ethyl acetate to form homogenous solution A. Likewise, 3,3-Dimethylacrylic acid, trimethylamine, and ethyl acetate were mixed to form solution B. Thereafter, the solution B was gently poured into solution A dropwise at 60 °C with continuous stirring. The reaction was carried out at 60 °C for 24 hours and the final product was subsequently and repeatedly washed with ethanol and dried in an oven at 60 °C for 4 hours. The synthesized resist was then stored in a vacuum desiccator.

2.2 Thin film preparation

2 wt. % of the synthesized resist 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 film was prebaked at 100^oC for 60 sec.

2.3 Electron beam lithography (EBL): Electron Beam Lithography (EBL, e-Line PLUS model, Raith GmbH, Dortmund, Germany) was performed by the exposure of 18 KeV beam energy with various range of electron doses over ~40 nm thin resist film at the current ~22.3 pA using ~10 µm aperture.

2.4 Helium ion Beam Lithography (He^+BL)

He^+BL (Zeiss ORION Nano Fab system) was performed with 30 KeV He^+ beam on ~40 nm thin resist film at the current ~ 0.4 pA using ~10 µm numerical aperture. After being exposed with He^+ beam and e-beam, negative tone patterns were developed in MIBK: IPA mixture in the ratio of 1:3 vol/vol where the exposed thin films were dipped for 1 min 15 sec.

2.5 Characterization

Field emission scanning electron microscopy (FESEM, Zeiss, Gemini SEM 500, Germany) was used to scan the nano-patterns. The particle size distribution of Ni-DMA resist was analysed by dynamic light scattering (Zetasizer Nano-ZS, Malvern Panalytical) method. Surface functional groups were identified by Fourier transform infrared spectroscopy (FTIR, Carry 600 Series, atomic force microscope (AFM) (Bruker Icon) was used to analyse the film thickness. The LER and LWR parameters for exposed line-patterns were measured by industry-standardized metrology software SuMMIT®.

3. RESULTS AND DISCUSSION.

The Ni-DMA MCOC resist material was synthesized by the reaction of nickel salt with monovalent organic ligand (3,3-Dimethylacrylic acid) in the presence of ethyl acetate and tri ethyl amine at 65 °C for 24 h. The synthesized resist material was easily soluble in ethyl lactate solvent.

3.1 High-resolution pattern and etch resistance analysis for Ni-DMA MCOC resists

To achieve high-resolution single-digit patterning, the spin-coated ~40 nm thick Ni-DMA, MCOC resists were exposed under the He^+ beam and e-beam by covering a broad range of doses. After being irradiated under He^+BL and EBL, the

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polarity of the resists was changed from polar to non-polar. Therefore, the unexposed regions of the exposed resists film got dissolved in a polar solvent, which is MIBK: IPA (1:3 v/v), while the remaining exposed resist was examined by FESEM and showed the negative tone characteristics in the form of line-patterns.

After the exposure under He^{+}BL system, the Ni-DMA, MCOC exhibited well-resolved high-dense features of ~12 nm lines with the line-space ratio of 1:1, as shown in Figure 1(a). Also, the high resolution sub-10 nm patterns with the features of L/2S, L/3S and L/4S, at the dose of 40 μC/cm^2, showed in Figure 1(b-d), reveals the ability of the formulated resists to generate sub-10 nm features. To support our claims, the Ni-DMA resists were also exposed under the EBL system and proved its capability of patterning high-resolution dense features as indicated in Figure 1(e-f). Also, the minimum features of ~9 nm patterned using EBL confirmed that the sub-10 nm resolution ability of newly developed resists formulation as showed in Figure 1(g). Moreover, Figure 2, evidently demonstrates the potential of the developed resists by patterning highly dense dot arrays of ~40 nm as depicted in the form of IIT-Mandi logo and also the sharp edged development in ~200 nm complex alphaneumaric structure (C*4*DFED) reveals its ability to generate large-area complex designs as per the user's requirement.

Although, the formulation for metal core clusters resists was accomplished by considering Nickel (metal):DMA (ligand) of 1.28 : 1, these higher metal contents in the Ni-DMA, MCOC resists boost the irradiation activation rate of the resists during the exposure and made it more sensitive to the irradiated He^{+} beam. Even though, DMA as a weak ligand results in ease displacement[6,8] after being exposed under He^{+}BL at ~40 μC/cm^2 and consequences the defect-free sub-12 nm patterns at considerably lower He^{+} beam dose.

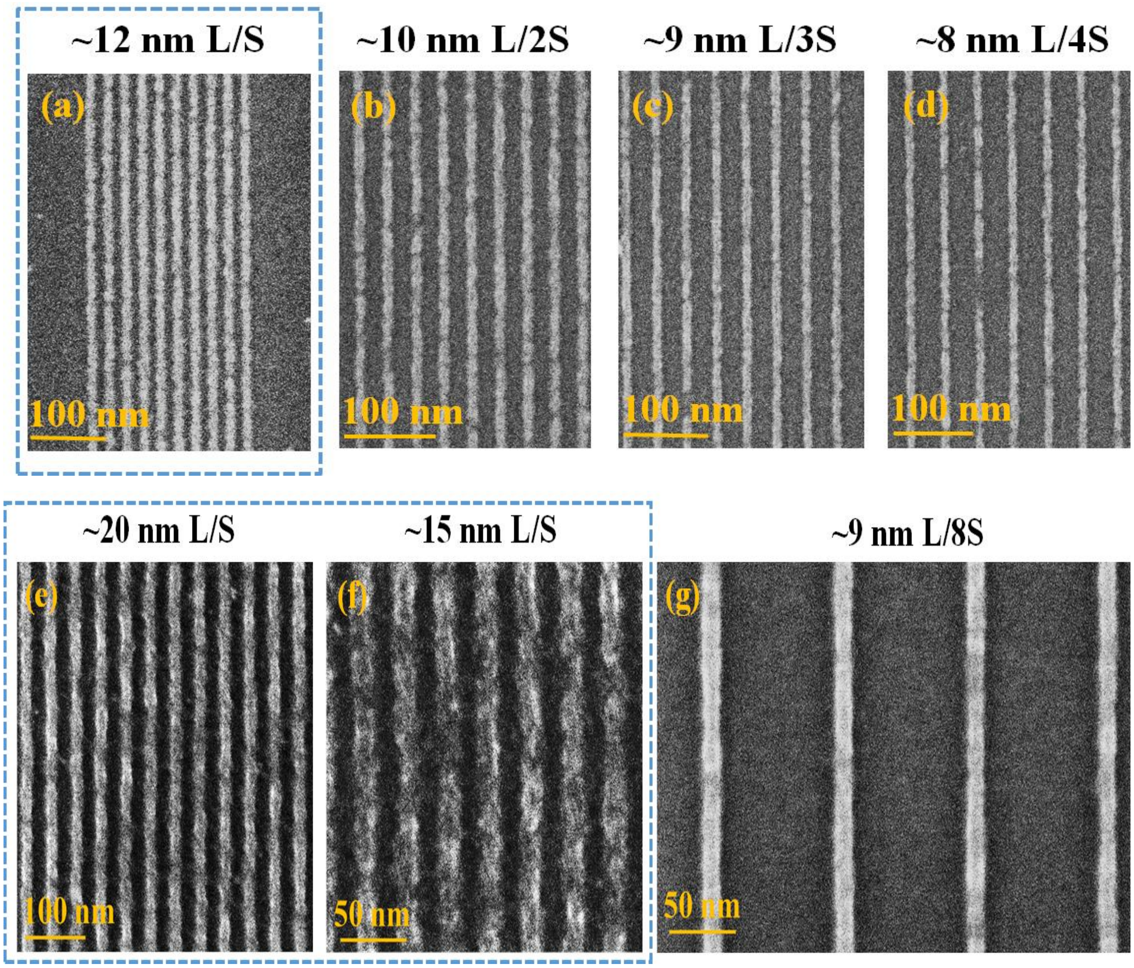

Figure 1. FESEM images of exposed Ni-based MCOC resist, using He^{+}BL (a) 12 nm L/S (b) 8 nm L/2S patterns and (c) 8 nm L/4S at the dose 40 μC/cm^2, and using EBL (e)-(f) ~14 nm L/S and (g) ~9 nm L/5S at the dose of ~1400 μC/cm^2.

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The contrast curve of Ni-DMA, MCOC resists films were examined with 30 KeV He^+ beam exposure for various doses ranging from of 1 to 70 µC/cm^2 and also with the 18 KeV, e-beam for dose, ranging from 1 to 1100 µC/cm^2 as represented in the contrasts curves of Figure 3(a). In the case of He^+BL the contrast (γ_{HIBL}) and sensitivity (E_{HIBL}) for the formulated resists were 2.325 and 35.04 µC/cm^2, respectively, while for the EBL, the contrast (γ_{EBL}) and sensitivity (E_{EBL}) were calculated as 1.32 and 620 µC/cm^2. However, the minimum He^+ dose required to accomplish the high-resolution defect-free line patterns is ~40 µC/cm^2, which is typically ~35 times lesser dose than the EBL exposure dose used to pattern well developed high-resolution line features. Moreover, novel Ni–DMA, MCOC resists sensitivity (EBL and He+BL both) were noticed better than earlier hybrid resists reported elsewhere.[9]

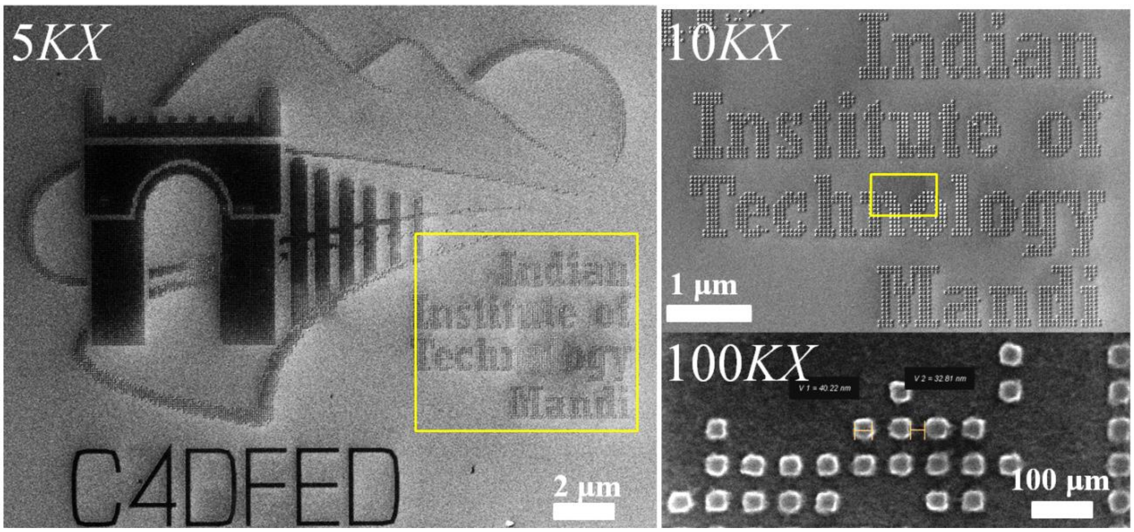

Figure 2. FESEM images of EBL exposed complex structure (IIT-Mandi logo) with 40 nm/pixels for logo.bmp and developed ~ 200 nm alphanumeric sharp-edge structure over Ni-based MCOC resist

The newly developed Ni-DMA, MCOC resists also displays a well trade-off between critical dimension (CD), sensitivity and average line-and-width roughness by patterning sub-10 nm features CD at ~40 µC/cm^2 with the considerable lower LER and LWR of 2.16 ± 0.04 nm and 3.03 ± 0.06 nm, respectively as compute for the Figure 1(d). Though, in the case of dense line-patterns, the LER and LWR increases as the feature size decreases and the maximum LER and LWR of 3.27 ± 0.13 nm and 3.64 ± 0.17 nm, respectively, were observed in the case of ~12 nm L/S line-patterns as indicated in Figure 3(b). It demonstrates the LER and LWR vs feature size variation for high-resolution L/S features. The further reduction in LER and LWR, beyond ~2 nm, especially for high-resolution dense patterns may be realized with better process optimization of the resist formulations.

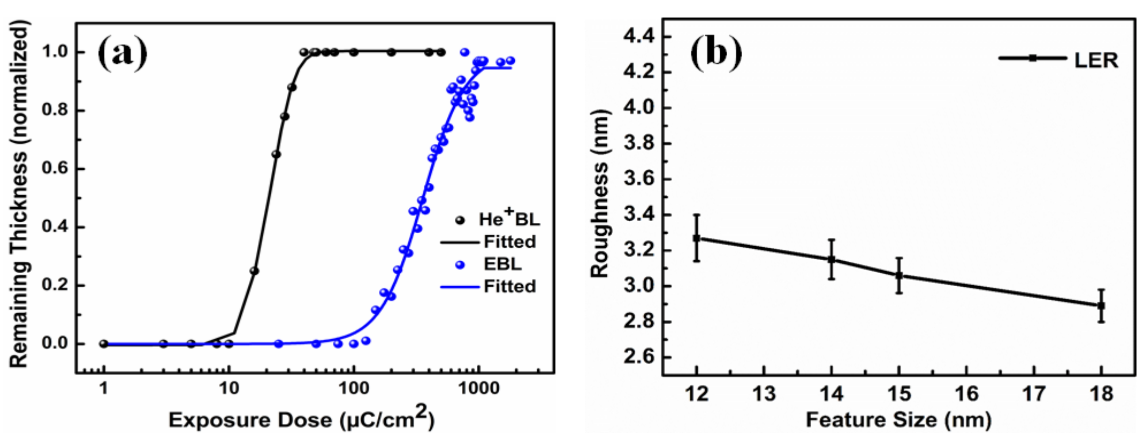

Figure 3. (a) Remaining Thickness vs He^+ beam doses characteristics for Ni-DMA MCOC resist, and (b) LER variations with respect to the CD of high dense line patterns.

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To adapt to potential candidature for Ni-DMA, MCOC resists to upfront high-volume manufacturing (HVM) of silicon technology, the resists etch resistance is needed to be systematically established. Where significantly moderate etch resistance of resists material w.r.t silicon is always desirable. Here, we compared the etch rate of the Ni-DMA MCOC resists formulation with the silicon wafer with (SF6-) etching environment. The etching precursor (SF6) gas flowed over the resists thin film samples with rate of 25 sccm and at 1.5 mTorr with RF power of 60 Watt. Thereafter, different samples were collected at intervals of 10 seconds to characterize the etch rate of the resists films. The etch rates for the Ni-DMA MCOC resists and silicon at the above-mentioned recipe were evaluated by measuring the thicknesses before and after the reactive ion etching using AFM. The etch rate for the Ni-DMA resists and silicon was found to be ~0.045 nm/sec and 0.6 nm/sec, respectively. Figure 4 shows the etch ratios of the Ni-DMA, MCOC resists w.r.t the silicon at 10 sec, 20 sec, 30 sec, 40 sec, 50 sec, and 60 sec, subsequent intervals.

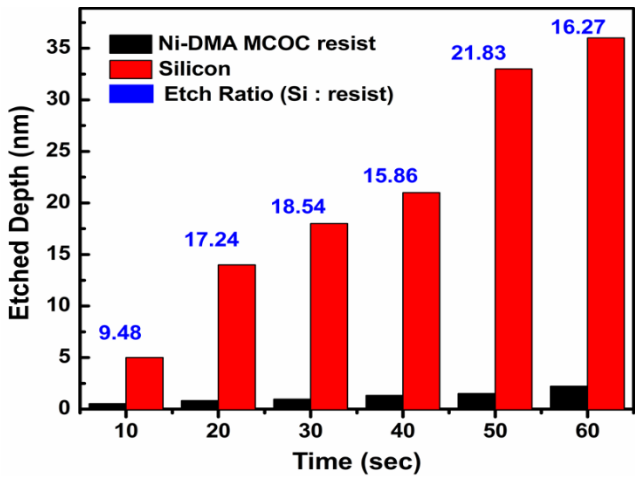

Figure 4. Etched depth with respect to the time for the Ni-DMA MCOC resist and the silicon wafer

3.2 Cluster Size Analysis

The average cluster size of Ni-DMA, MCOC resists was characterized by the Dynamic Light Scattering (DLS) method. Figure 5(a) shows the particle size distribution curve which signifies the average particle size of ~ 1.72 nm. Such a small particle size of Ni-DMA, MCOC resists suggests that cluster formation of nickel metal with DMA ligand. Also, this small size distribution of Ni-DMA clusters is too responsible for sub-12 nm dense line pattern formation by He^{+}BL with acceptable LER and LWR which is way better than the metal oxide resists with broad particle size distribution.[10,11,12]

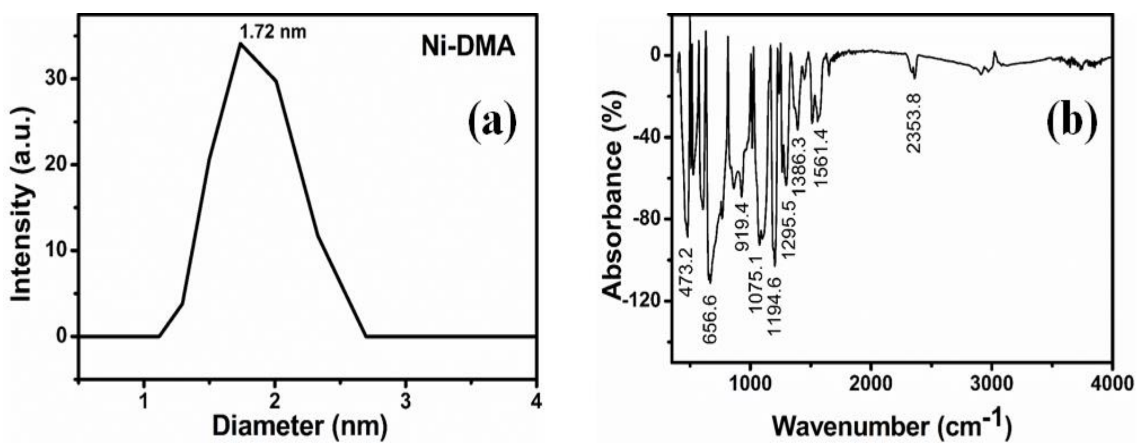

Figure 5. (a) Average cluster size distribution and (b) FTIR of the formulated Ni-DMA MCOC resist.

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3.3 FTIR Analysis

The presence of the various functional groups in Ni-DMA, MCOC resists is analyzed by FTIR and the results are displayed in Figure 5(b). The Peak observed at 473.2 cm^{-1} corresponds to the stretching vibration of Ni-O bonds formed in Ni-DMA, MCOC resists.[13] The peaks obtained at 1075 and 1194.6 cm^{-1} corresponds to C-O stretching. Additionally, the peak observed at 1386.3 cm^{-1} and 1561.4 cm^{-1} corresponds to the C-H bending and C=C bending, respectively. Whereas, the peak identified at 2353 cm^{-1} is representing the O=C=O stretching.

4. CONCLUSIONS.

In summary, we newly developed the metal core organic clusters (MCOC) resists using nickel as a metal-binding unit that can absorb a large fraction of incident charge or photon energy and DMA as a weak ligand that can result in ease ligand displacement after being exposed at low dose. The analysis shows that patterns with sub-10 nm features along with highly dense sub-12 nm lines with the acceptable LER and LWR parameters i.e. 2.16 ± 0.04 nm and 3.03 ± 0.06 nm, respectively, are obtained at the He^+ dose ~40 $\mu C/cm^2$. The e-beam exposure analysis confirms the ability of Ni-DMA, MCOC resists to pattern the sub-10 nm line features ~9 nm, as well as, sub-15 nm L/S line features at the exposure dose of ~1400 $\mu C/cm^2$ i.e. 35 times higher than the He^+ beam exposure dose. The Ni-based MCOC resists showed promising lithographic performance under He^+ ion irradiation with the additional advantages of high etch resistance i.e. of ~15 times w.r.t Si and highly dense patterns of ~12 nm. All these studies evidently support the application of newly formulated Ni-DMA, MCOC resists formulation as a potential EUV resists for the high volume manufacturing (HVM) of futuristic N7+ technology node.

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