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Satinder K. Sharma, Mohamad Ghulam Moinuddin, Pulikanti Guruprasad Reddy, Chullikkattil P. Pradeep, Subrata Ghosh, Kenneth E. Gonsalves, "Evaluation of high-resolution and sensitivity of n-CAR hybrid resist for sub-16nm or below technology node," Proc. SPIE 10583, Extreme Ultraviolet (EUV) Lithography IX, 105831Q (19 March 2018); doi: 10.1117/12.2297565

SPIE.

Event: SPIE Advanced Lithography, 2018, San Jose, California, United States

Evaluation of high-resolution and sensitivity of n-CAR hybrid resist for sub-16nm or below technology node

Satinder K. Sharma^{*1}, Mohamad Ghulam Moinuddin¹, Pulikanti Guruprasad Reddy², Chullikkattil P. Pradeep², Subrata Ghosh², and Kenneth E. Gonsalves^{**2}

¹School of Computing and Electrical Engineering, Indian Institute of Technology (IIT)-Mandi, (H.P), 175005, India.

²School of Basic Science, Indian Institute of Technology (IIT)-Mandi, (H. P), 175005, India.

ABSTRACT

MAPDST (4-(methacryloyloxy)phenyl)dimethylsulfoniumtrifluoromethanesulfonate)) based resist analogues are reported to pattern high-resolution nano features (20 nm) under wide range of lithography tools including electron beam lithography (EBL), extreme ultraviolet lithography (EUVL), 193 nm immersion lithography etc. However, these resists have not yet patterned lower node features, especially at sub-15 nm regime with ultra-low line edge roughness (LER) and line width roughness (LWR). One of the methods to improve the resolution of a resist is the structural modification. Towards this, we have developed two new hybrid copolymer resists i.e MAPDST-co-ADSM and MAPDST-co-TPMA by the copolymerization of radiation sensitive organic MAPDST with hybrid tin monomers ADSM and TPMA (ADSM = acetyldibutylstannyl methacrylate; TPMA = triphenyl tin methacrylate) for high-resolution EBL applications. The developed resists were studied for their sub-15 nm line patterns with low LER and LWR features. Various line features, starting from 30-12 nm with different line/space (L/S to L/10S) characteristics were studied at various e-beam doses 200-1200 $\mu\text{C}/\text{cm}^2$. Isolated 12 nm line features have been achieved with the resist MAPDST-co-ADSM at a dose 1200 $\mu\text{C}/\text{cm}^2$. Meanwhile, the MAPDST-co-TPMA resist patterned 15 nm features at the dose 700 $\mu\text{C}/\text{cm}^2$. The estimated sensitivity and contrast of resists MAPDST-co-ADSM and MAPDST-co-TPMA were 1.60; 450 $\mu\text{C}/\text{cm}^2$ and 1.55; 380 $\mu\text{C}/\text{cm}^2$ respectively. Similarly, the computed LER and LWR parameters exhibited by the resists MAPDST-co-ADSM and MAPDST-co-TPMA for sub-30 nm features were 0.99; 1.22 and 1.8; 3 nm respectively. The e-beam studies revealed a resolution enhancement of the hybrid resists at 12 nm regime as compared to the neat poly(MAPDST) resist (where the resist resolution was 20 nm) indicating improvements in the lithography properties of these resists.

Keywords: Non-chemically amplified resist, Electron beam lithography, Extreme ultraviolet lithography, Critical dimension, Line edge roughness, Line width roughness.

1. INTRODUCTION

Extreme ultraviolet lithography (EUVL) is a leading next-generation lithography technique for the semiconductor industry that has the capability to achieve 7 nm node or below features^[1,2]. Therefore, for the realization of high density integrated circuits (IC) manufacturing, significant improvements of EUV resists are essential^[2]. It is known that efficient photoresists for high-resolution EUVL should possess the following characteristics: low line edge roughness (LER), low line width roughness (LWR), high sensitivity, high resolution, high etch resistance and the capability to develop collapse free patterns with the aqueous base developer^[3,4]. Although, a number of organic photoresists based on the chemical amplification (CAR)^[5,6] and non-chemical amplification (n-CAR)^[7-11] principles are reported for sub-20 patterning studies, many of such resists immensely suffer from the lower resolution, sensitivity and etch resistance properties. The inclusion of inorganic entities such as metaloxide nanoparticles, metaloxide clusters, organo-metallics etc. in a neat organic photo resists formulation can enhance the resolution, sensitivity, etch resistance and thermal stability properties^[10-14]. Therefore, development of new photoresists or modification of existing resists for improved lithography applications is an important research area^[2]. Our group has focused on the development of sulfoniumtriflate based MAPDST (MAPDST = (4-

(methacryloyloxy)phenyl)dimethylsulfoniumtrifluoromethanesulfonate) resists for high-resolution lithography applications^[2]. One of the significant advantages of sulfonium triflate based resists involves the use of industrial standard developer TMAH for negative tone patterning^[2]. By using MAPDST as a radiation sensitive backbone, poly(MAPDST) resist was developed for 20 nm line patterning under electron beam (e-beam) and EUV lithography conditions^[15-17]. Furthermore, our group has also developed a number of other novel resists for next generation e-beam and EUV lithography application.^[15-16]

Therefore, in order to improve sensitivity and resolution of the poly(MAPDST) toward sub-10 nm regime, the present study focused on the design and synthesis of two new hybrid copolymer resists i.e. MAPDST-*co*-ADSM and MAPDST-*co*-TPMA for e-beam lithography applications. The MAPDST is copolymerized with the hybrid tin sensitizers such as ADSM (acetyldibutylstannyl methacrylate) and TPMA (triphenyltin methacrylate) in order to get sensitive hybrid copolymers with better resolution. Tin is having a high optical density (8-10) as compared to that of carbon (0.2), therefore, the synthesized resists are expected to harvest photons/radiations better towards high energy lithography applications. During lithography exposure, the resist undergoes structural changes from hydrophilic sulfonium triflate to hydrophobic aromatic sulfide functionality leading to polarity switching resulting in negative tone patterning. The detailed e-beam lithography studies and nano-patterning investigations of these resists are discussed in the following sections.

2. EXPERIMENTAL DETAILS

2.1 Resist synthesis and thin film preparation

The hybrid copolymer resists MAPDST-*co*-ADSM and MAPDST-*co*-TPMA were synthesized through free radical polymerization pathway by the reaction between organic monomer MAPDST and tin hybrid monomers ADSM and TPMA by using AIBN as a free radical initiator in acetonitrile/tetrahydrofuran (ACN/THF) (1:1) at 65 °C for 2 days. The chemical structures of the MAPDST-*co*-ADSM and MAPDST-*co*-TPMA copolymers are given in Figure 1. The synthesized polymers were thoroughly characterized by using the NMR, IR, GPC, TGA and EDX spectroscopic techniques. The calculated molecular weight (Mw) and poly-dispersity index (PDI) of copolymers MAPDST-*co*-ADSM and MAPDST-*co*-TPMA were 8221 g/mol, 1.51 and 6933 g/mol, 2.06 respectively. The resist formulations were prepared by dissolving the solid copolymers (2 wt %) in acetonitrile solution followed by filtering through 0.2 μm Teflon filters in order to get a particle-free solution.

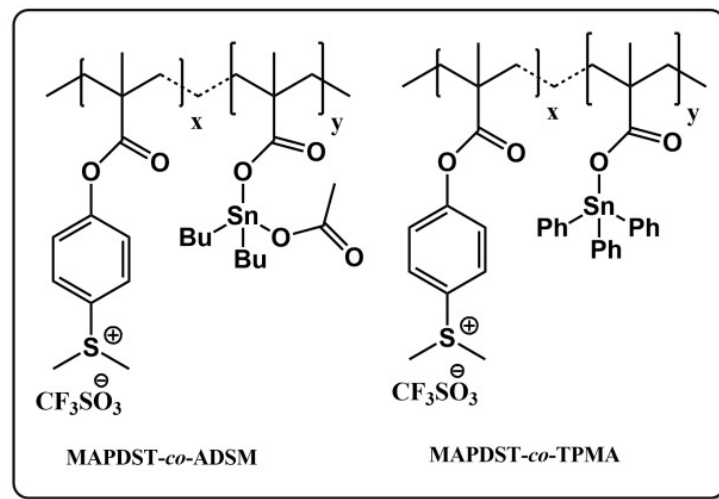


Figure 1 Chemical micro-structure of the MAPDST-*co*-ADSM and MAPDST-*co*-TPMA hybrid copolymers.

The defect-free thin films with the thickness ~ 30 nm of resists were achieved by spin coating the resist solutions onto a 2-inch p-type silicon substrate at 4500 rpm speed for 60 sec. Later, the resist coated thin films were subjected to pre-exposure bake at 90 °C for 60 sec. After e-beam assessment, the resist thin films were subjected to post-exposure bake at 70 °C for 60 sec. Finally, the negative tone nano-features of resists were achieved after the development of resist films with aqueous 0.022N TMAH developer for 30 sec.

2.2 E-beam lithography parameters

The characterized resist thin films were subjected to electron beam lithography studies. We used Raith eLine PLUS exposure tool with the beam spot size 2 nm for 10 nm line patterning investigations. In order to focus the e-beam radiations, 10 μm aperture was used at 20 KeV voltage. Various exposure doses starting from 10 $\mu\text{C}/\text{cm}^2$ to 1200 $\mu\text{C}/\text{cm}^2$ were tested for the dose analysis and nano-patterning investigation.

3. RESULT AND DISCUSSION

3.1 Thin film evaluation

In order to get film thickness ~ 30 nm, the hybrid copolymer resists MAPDST-co-ADSM and MAPDST-co-TPMA were spin-coated with different spinning parameters (Figure 2 (a)). As shown in Figure 2 (a), the thickness of the resist thin films depended on the RPM used, which revealed that 4500 rpm was the best condition for ~ 30 nm film thickness. The obtained smooth, defect-free thin films of hybrids were characterized by using high-resolution atomic force microscopy (Figure 2 (b & c)). The calculated RMS roughness of the smooth thin films obtained from MAPDST-co-ADSM and MAPDST-co-TPMA resists were 0.27 nm; 0.55 nm. The roughness analyses revealed that the patterned thin films are well suitable for nano-lithography applications.

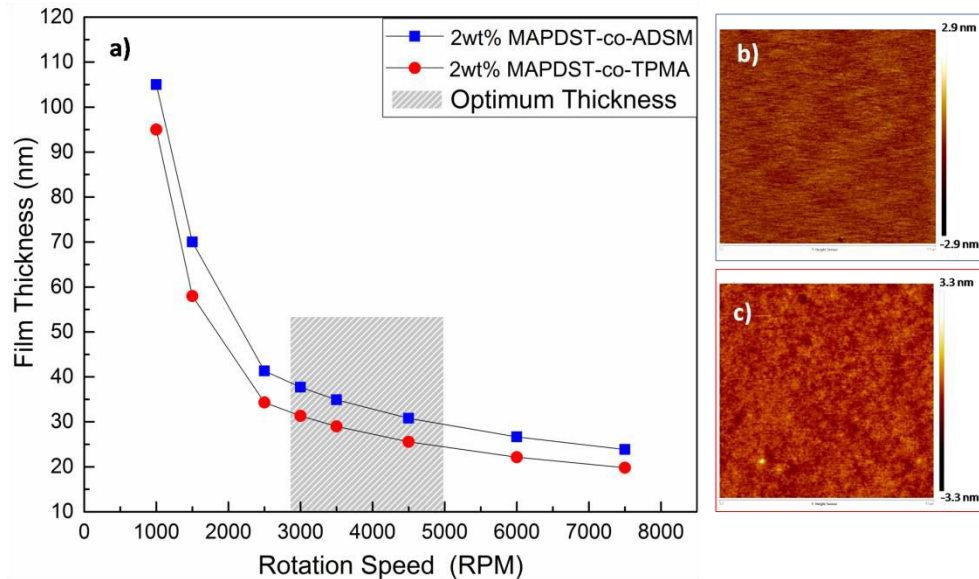


Figure 2 a) Thin film optimization of MAPDST-co-ADSM and MAPDST-co-TPMA resists at different spinning parameters ; b) AFM thin film image of MAPDST-co-ADSM resist (roughness = ~ 0.27 nm); c) AFM thin film image of MAPDST-co-TPMA resist (roughness = ~ 0.55 nm).

3.2 E-beam lithography studies

The smooth thinfilms of hybrid copolymers MAPDST-*co*-ADSM and MAPDST-*co*-TPMA were exposed to e-beam radiations with different doses starting from 200 $\mu\text{C}/\text{cm}^2$ –1200 $\mu\text{C}/\text{cm}^2$ at 20 KeV. This systematic dose analyses revealed that the patterning of sub-15 nm features is dependent on the e-beam exposure dose used for these hybrids. A plot between the minimum line features (10-100 nm) obtained vs the different line/space characteristics (L/5-L/10S) of resists at different e-beam doses (200-1200 $\mu\text{C}/\text{cm}^2$) is given in Figure 3. These studies revealed that the minimum feature size achieved in the case of hybrids MAPDST-*co*-ADSM and MAPDST-*co*-TPMA are 12 nm and 15 nm at doses 1200 and 700 $\mu\text{C}/\text{cm}^2$ respectively (Figure 4).

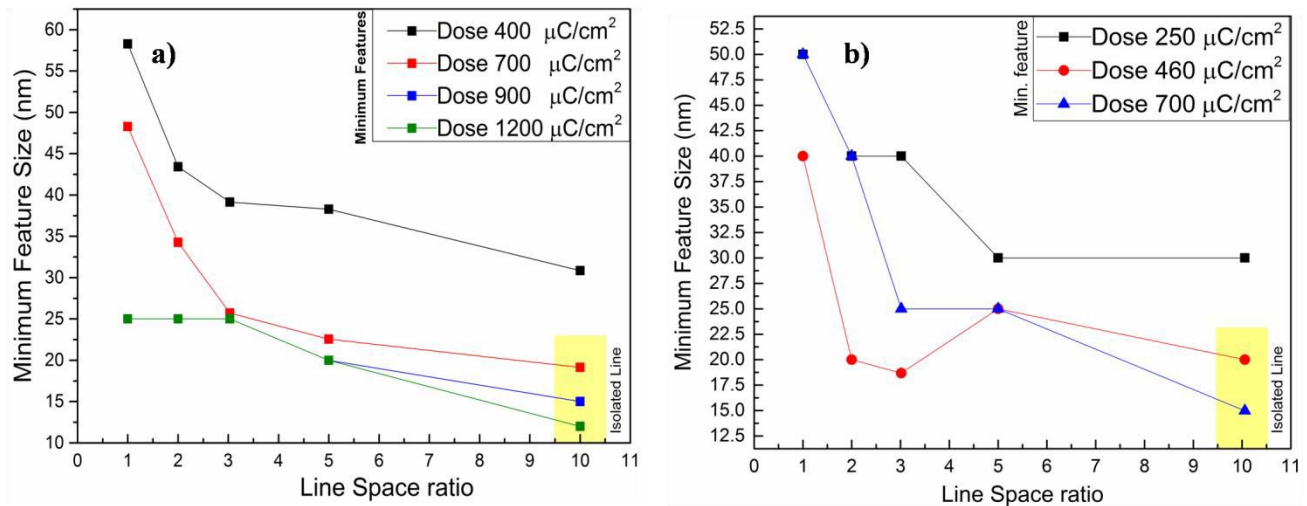


Figure 3 The plot between minimum feature size vs various line/space features (L/S to L/10S) exhibited by resists (a) MAPDST-*co*-ADSM and (b) MAPDST-*co*-TPMA at various doses (200-1200 $\mu\text{C}/\text{cm}^2$).

Various line patterns (12, 15, 18, 20, 25, 30 nm etc.) with different line/space (L/S-L/10S) characteristics exhibited by the hybrid resists were characterized by using FESEM technique and are shown in Figure 5. For example, the high resolution 25 and 30 nm line patterns with L/S and L/2S (line/space) features obtained from the resist MAPDST-*co*-ADSM at different doses 900 $\mu\text{C}/\text{cm}^2$ and 700 $\mu\text{C}/\text{cm}^2$ are shown in Figure 5 (a-b & e-f). In addition, the 50 nm and 80 nm (line/space) features are shown in Figure 5 (c-d). Moreover, the high resolution and isolated line patterns such as 12 nm and 15 nm feature exhibited by the resist MAPDST-*co*-ADSM at the dose 1200 $\mu\text{C}/\text{cm}^2$ are shown in Figure 5 (g & h). Likewise, the 40 (L/S), 50 (L/S), 18 nm (L/2S), 30 nm (L/2S), 18 nm (L/4S) and 20 nm (L/4S) line features patterned by the resist MAPDST-*co*-TPMA at various doses are shown in Figure 5 (i-n). In addition, the high-resolution isolated line patterns such as 15 nm and 25 nm exhibited by the resist MAPDST-*co*-ADSM at low exposure doses 700 and 460 $\mu\text{C}/\text{cm}^2$ were shown in Figure 5 (o & p). The SEM analysis revealed that both the hybrid resists are sensitive in nature and are able to pattern collapse-free nano-features even at sub-15 nm regime. As noticed from Figure 5 (o), the high resolution 15 nm line features exhibited by the resist MAPDST-*co*-TPMA is achieved at the dose range 700 $\mu\text{C}/\text{cm}^2$. While, similar line features exhibited by the MAPDST-*co*-ADSM resist were achieved at the dose 1200 $\mu\text{C}/\text{cm}^2$, indicating a high sensitivity of MAPDST-*co*-TPMA resist compared to MAPDST-*co*-ADSM resist (Figure 5(h)). Similarly, MAPDST-*co*-ADSM resist patterned 12 nm isolated lines (Figure 5(g)), while, the resist MAPDST-*co*-TPMA was unable to pattern such lower node features probably due to the resolution limit of the resist. The results were also compared to our previously published neat poly(MAPDST) resist, which revealed improved resolution of the newly developed hybrids (MAPDST-*co*-ADSM and MAPDST-*co*-TPMA) than the neat poly(MAPDST) resist^[16-17]. This might be due to the effect of the hybrid tin entities in the resist structure, which might have caused the resolution enhancement. The LER and LWR parameters of resists

MAPDST-*co*-ADSM and MAPDST-*co*-TPMA were calculated from the SUMMIT metrology software. The 30 nm line patterns were considered for these calculations. The obtained LER and LWR values for MAPDST-*co*-ADSM and MAPDST-*co*-TPMA resists were 0.99; 1.22 and 1.8; 3 nm respectively, which are found to be better than those of a few e-beam resists reported earlier.^[18]

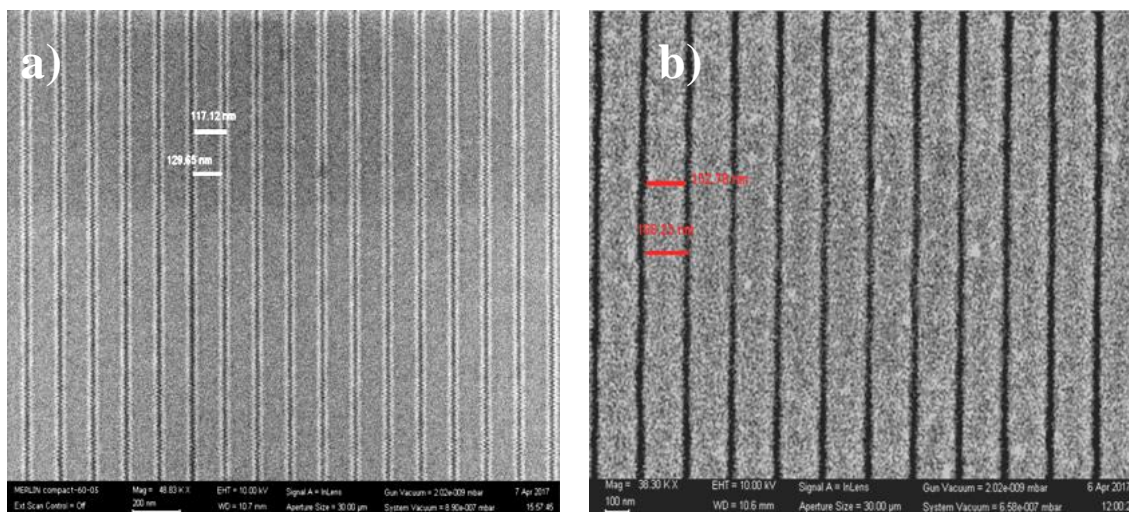


Figure 4 High-resolution FE-SEM top-down images of (a) MAPDST-*co*-ADSM copolymer resist with 12 nm line features; (b) MAPDST-*co*-TPMA copolymer resist with 15 nm line feature.

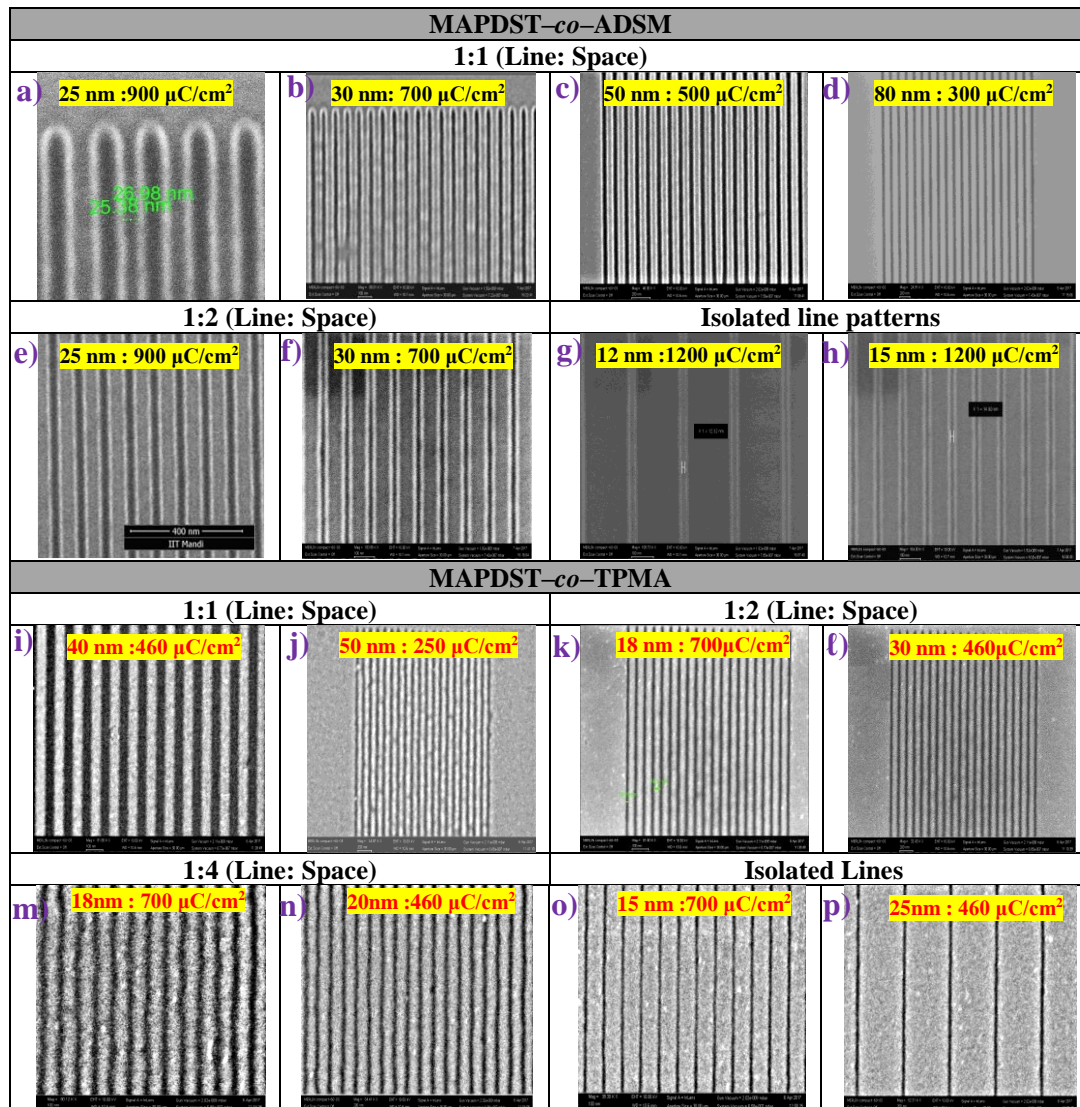


Figure 5 e-Beam exposed line patterns of MAPDST-co-ADSM and MAPDST-co-TPMA copolymer resists at different exposure doses

3.3 Contrast curve analysis and LER calculations

The contrast and sensitivity of the hybrid copolymer resists MAPDST-co-ADSM and MAPDST-co-TPMA were studied by using normalized remaining thickness (NRT) curve analysis. NRT is a plot between the residual thickness vs various e-beam exposure doses of a resist^[19]. We considered the residual thickness of 30 nm line features patterned from the hybrid copolymer formulations at different e-beam doses starting from 10 $\mu\text{C}/\text{cm}^2$ to 900 $\mu\text{C}/\text{cm}^2$ for the NRT analysis. In order to measure the remaining thickness of the patterned resist features, AFM line profile based technique with the standard cantilever tip (TESPA) was used. The NRT profile for the hybrid copolymer resists is shown in Figure 6. As depicted in Figure 6, the thickness of the resist increases gradually with the exposure dose, indicating the negative tone nature of the developed hybrid resist formulations. The computed contrast and sensitivity of the hybrid copolymer resists MAPDST-co-ADSM and MAPDST-co-TPMA were 1.60; 450 $\mu\text{C}/\text{cm}^2$ and 1.55; 380 $\mu\text{C}/\text{cm}^2$, respectively. The sensitivity studies further confirmed our earlier observation of high sensitivity of MAPDST-co-TPMA resist as compared to MAPDST-co-ADSM resist. The sensitivity exhibited by the hybrid resists was also compared with a few of the existing resist systems.

The popular commercial inorganic resist HSQ is reported to pattern 50 nm wide line features at the e-beam dose 1000 $\mu\text{C}/\text{cm}^2$ ^[20]. Similarly, the inorganic ZircSOx resist was developed for e-beam lithography applications for patterning 15 nm line features at the dose 999 $\mu\text{C}/\text{cm}^2$ ^[21]. These comparative studies reveal that the sensitivity exhibited by the current resists are quite good.

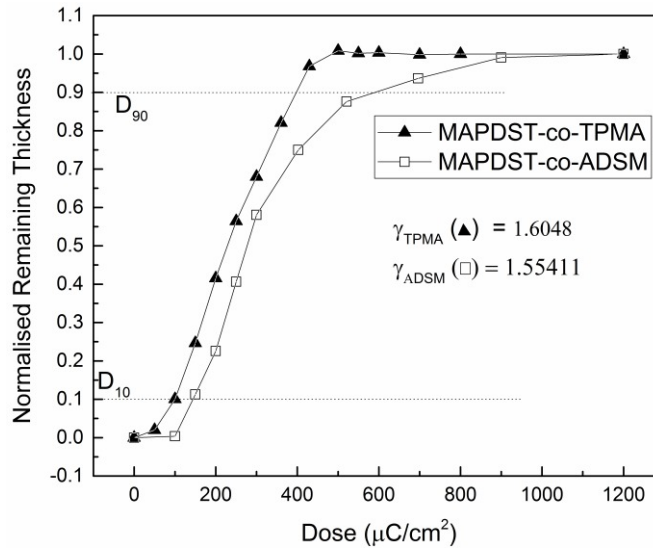


Figure 6 NRT vs dose characteristics of the hybrid copolymer resists MAPDST-co-ADSM and MAPDST-co-TPMA

As reported, sulfoniumtriflate based resists are sensitive towards radiations^[15-17,19]. A major part of the hybrid copolymers MAPDST-co-ADSM and MAPDST-co-TPMA consist of the radiation sensitive sulfoniumtriflates of MAPDST. During the lithography process, the polar sulfoniumtriflates of MAPDST undergo structural transformations from polar sulfoniumtriflates to non-polar aromatic sulfide functionality^[17]. Therefore, resists offer the negative tone patterning upon developing the exposed resist thin films with an aqueous base developer such as TMAH. Aqueous TMAH developer dissolves essentially the unexposed polar portion of the resist while leaving behind the exposed non-polar portions intact. Brinard *et al.* reported several tin-based resists for high resolution EUV lithography applications^[12]. They reported patterning mechanism of resists involve by cleaving tin-carbon bond toward high energy lithography radiations. Similarly, the tin-carbon bonds in the hybrid resists MAPDST-co-ADSM and MAPDST-co-TPMA will also propose to get cleave for quick polarity conversions. Our previous reports on poly(MAPDST) resist for EBL and EUVL studies had revealed its patterning capability of sub-20 nm features with moderate sensitivity. Due to the inclusion of inorganic tin entities such as ADSM and TPMA in the poly (MAPDST), resist resolution of the resultant hybrid copolymers (MAPDST-co-ADSM and MAPDST-co-TPMA) got enhanced from sub-20 nm to sub-10 nm features, which is a desirable outcome of this study. Considering all these, the present photo resists are expected to pattern sub-10 nm features for the next generation EUVL applications after further modifications.

4. CONCLUSIONS

We have developed two new hybrid n-CARs, i.e MAPDST-co-ADSM and MAPDST-co-TPMA, for high resolution e-beam lithography applications. Due to the inclusion of hybrid tin entities (ADSM & TPMA) in the poly(MAPDST), the resultant hybrid copolymers showed improved lithography properties, particularly for lower node sub-15 nm features. The various line patterns (30, 25, 20, 18, 15 and 12 nm) with different line/space (L/S-L/5S) features of resists were studied at different e-beam doses 200 $\mu\text{C}/\text{cm}^2$ -1200 $\mu\text{C}/\text{cm}^2$. The FESEM analysis showed the patterning of 12 and 15 nm features by the resists MAPDST-co-ADSM and MAPDST-co-TPMA at e-beam doses 1200 and 700 $\mu\text{C}/\text{cm}^2$ respectively. The sensitivity and contrast of resists MAPDST-co-ADSM and MAPDST-co-TPMA were calculated from the contrast curve

analysis as 450 $\mu\text{C}/\text{cm}^2$; 1.6 and 380 $\mu\text{C}/\text{cm}^2$; 1.55 respectively. In order to calculate the LER and LWR, the 30 nm line features exhibited by resists MAPDST-*co*-ADSM and MAPDST-*co*-TPMA were analysed by SUMMIT package and were calculated as 0.99; 1.22 and 1.8; 3 nm respectively. All the studies conclude that the newly developed resists are suitable for futuristic EUV lithography applications. Currently, we are engaged in exploring EUVL performance of these resists at sub-10 nm regime and the results will be published subsequently as part of the extended work.

5. ACKNOWLEDGEMENT

Authors thank the Department of Science and Technology (DST) and Technology Systems Development Program (TSDP), India for the financial support. Sanctioned project reference number: DST/TSG/AMT/2015/634. P. G. Reddy thanks the Council of Scientific and Industrial Research (CSIR), New Delhi, India for a senior research fellowship. M. G. Moinuddin thanks the Ministry of Electronics & Information Technology for a junior research fellowship under the Visvesvaraya Ph.D Scheme.

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