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Novel non-Chemically Amplified (n-CARs) Negative Resists for EUVL

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ABSTRACT

We report the lithography performance of novel non chemical amplified (n-CARS) negative photoresist materials which are accomplished by homopolymers and copolymers that are prepared from monomers containing sulfonium groups. The latter have long been found to be sensitive to UV radiation and undergo polarity change on exposure. For this reason, these groups were chosen as radiation sensitive groups in non-CARs that are discussed herein. Novel n-CAR negative resists were synthesized and characterized for EUVL applications, as they are directly sensitive to radiation without utilizing the concept of chemical amplification. The n-CARs achieved 20 and 16 nm L/2S, L/S patterns to meet the ITRS requirements. We will also discuss the sensitivity and LER of these negative n-CARS to e-beam irradiation which will provide a basis for EUVL down to the 16 nm node and below. These new negative tone resist provide a viable path forward for designing non-chemically amplified resists that can obtain higher resolutions than current chemically amplified resists at competitive sensitivities.

Keywords:- *non-Chemical Amplified Resist, LER, EBL, EUVL, Contrast, Sensitivity and Etch resistance*

1. INTRODUCTION

According to ITRS-2011, one of the major challenges for promoting EUV are the improvements in resist performance like sensitivity, resolution, etch resistance and line edge roughness (LER) to fulfill the demands of high-volume production.[1] The introduction of chemically amplified resists (CARs) has enabled the reduction in the half-pitch of patterned structures down to 22 nm in production because of their high sensitivity and resolution. However, CARS can limit the ultimate minimum hp resolution due to acid diffusion problems and post exposure instability especially for features at 16 nm and below,[2-5.] In addition to these effects, LER or LWR have become critical for sub 20 nm technology which do not meet the ITRS requirements based on CARs.[6-10] For that reason these must be controlled effectively. This places an additional constraint on the chemically amplified resist (CAR). Due to these shortcomings, recent attention has focused on the development of non-chemically amplified resists (n-CARs) for future lithography nodes.[11]

One such approach being investigated by us is the development of polymeric non- chemically amplified (n-CARs) negative photoresists for sub 20 nm technology. They are directly sensitive to radiation without utilizing the concept of chemical amplification (CARs). These resist designs are accomplished by homopolymers and copolymers that are prepared from monomers containing sulfonium groups. The latter have long been found to be sensitive to UV radiation and undergo polarity change-hydrophilic to hydrophobic in exposed regions only, acting as "negative tone" n-CARs. Thus n-CARs negative tone resists based on the copolymers poly(4-(methacryloyloxy)phenyl dimethylsulfonium triflate-co-methylmethacrylate) (Poly(MAPDST-co-MMA)), as well as the homopolymer are presented.

2. MATERIALS AND METHODS

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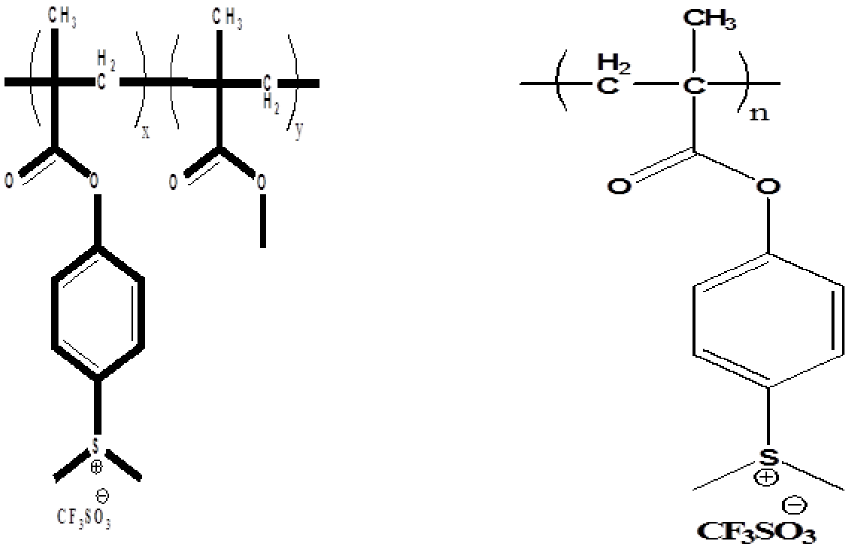
2.1 Materials

The monomer 4-(Methacryloyloxy)phenyl) dimethyl sulfoniumtriflate (MAPDST) was synthesized following literature procedure.[12-15] The resist, poly(MAPDST-co-MMA), was synthesized using AIBN initiated free radical cross polymerization between MAPDST and MMA (1 : 1 monomer feed ratio) at 60 °C under dry nitrogen atmosphere for 2 days. The molecular weight (M_w) of this co-polymer was calculated to be 4.3×10^3 by Gel Permeation Chromatography (GPC). The composition determined by ^1H NMR corresponds to $(MAPDST)_{75}(MMA)_{25}$. The T_g and T_m determined by DSC are 165 °C and 98−102 °C respectively. Similarly, MAPDST-homopolymer was synthesized by reacting monomer MAPDST and using AIBN as initiator of 1 wt% relative to monomer in acetonitrile at 60 °C underneath dry nitrogen atmosphere for 2 days. Its chemical structure is shown in Fig 1(b). Both the resist materials were obtained as white crystalline solids. The synthesized resist materials were characterized using FT-IR, ^1H NMR, DSC-TGA analysis and the details are given in our upcoming research papers.[16] The molecular weight of the above copolymer (M_w= 10.8×10^3) was calculated using GPC analysis.



(a) MAPDST –MMA Copolymer (b) MAPDST –Homopolymer

Figure 1. Designed resist molecules - Structure of (a) MAPDST-MMA copolymer (x=75, 7=25) and (b) MAPDST-MMA homopolymer

2.2 Resist solution

The resist solutions of the synthesized polymers were prepared in methanol at 3% by weight depending on the molecular weight of solid resist polymers and filtered through a 0.2 μm Teflon filter to remove particles.

2.3 Lithographic evaluation using an E-Beam Exposure

To prepare thin films for e-beam lithography experiments the photoresist solutions were spin coated directly on HMDS treated RCA cleaned bare p-type Si wafer pieces of 2 cm by 2 cm in size to obtain a thickness of 50 nm and then baked on a hot plate to remove any excess solvent. Resist coated samples were pre-exposure baked (PEB) at 100 ºC for 120 s and 90 ºC for 90 s for MAPDST-homopolymer and MAPDST-MMA copolymer respectively. Exposures were carried out by using Raith GmbH, 150-Two model machine (e-beam) at the exposure energy of 20 KeV by covering a broad range of doses. The exposed samples were developed in optimized developer TMAH-1(aqueous solutions of TMAH in DI water maintained pH around 11.5) at room temp for 20 seconds, rinsed in de-ionized water for about 10 to 15 seconds and blow dried with pure nitrogen gas.

2.4 EUV Lithography evaluation

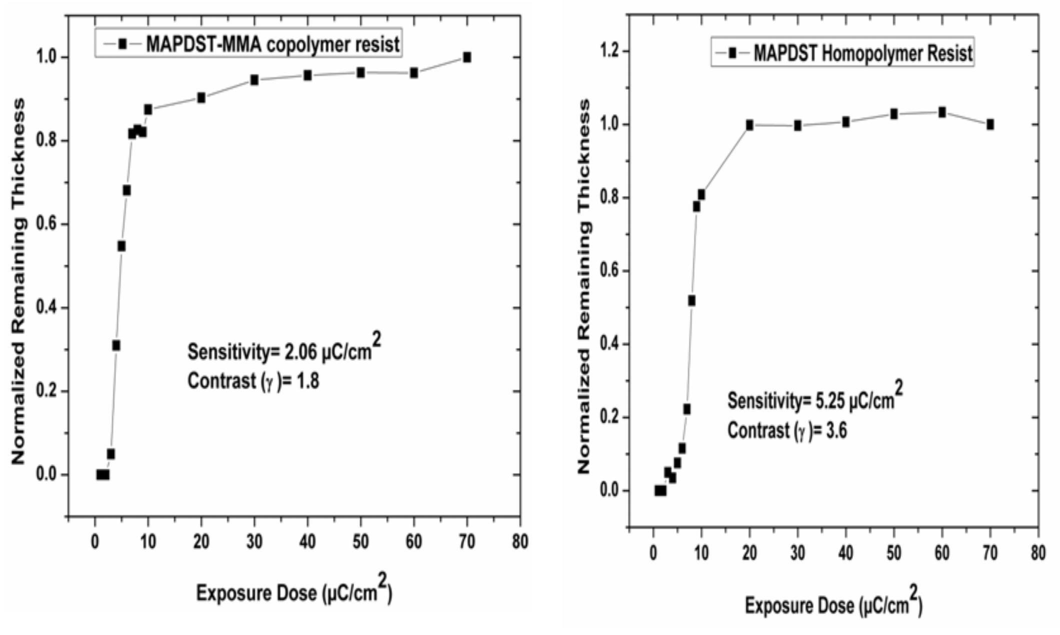
The resist solutions were prepared in methanol and filtered by 0.2 micron Teflon filter and spin-coated onto HMDS treated 200 mm silicon wafer for around 40 nm thin films before EUV exposure evaluation. The resist films of MAPDST-homopolymer and MAPDST-MMA copolymer were prebaked at 100 °C for 90 sec and 90 °C for 90 sec respectively. First Test wafers were run to calculate the E_o center dose value for both the resists layers. E_o center dose was obtained for MAPDST-MMA copolymer of 10 mJ/cm^2 and for MAPDST-homopolymer around 30 mJ/cm^2 but the actual value of E_o of MAPDST-homopolymer was not exactly determined and further exposures are planned. This material is highly dependent on developer conditions which further needs to be optimized for EUV radiations. The resulting photoresist layers were flood exposed with the respective E_o array using SEMATECH Berkeley Microfield Exposure Tool (MET) which is a high resolution EUV (13.5 nm) lithography tool. Samples were exposed using mask IMO228775 with Field of R4C3. The samples were post exposed baked at for 90 °C for 90 sec and 115 °C for 90 sec for MAPDST-homopolymer and MAPDST-MMA copolymer respectively. After the EUV exposure, these samples were developed with our optimized TMAH based developer named as TMAH-1 developer to obtain EUV E_o hence the photo speed. The exposed wafers were post exposure baked and developed with TMAH-1 solution to form nano features, line space patterns.

3. RESULTS AND DISCUSSION

The unexposed polymer thin film was polar in nature, due to its ionic character, consequently it is soluble in polar solvents such as water. Upon exposure to radiation, the polymer underwent a polarity change, as evidenced by its change in solubility after irradiation. Thus when irradiated, the anionic counter ions of the resist decomposed resulting in the formation of Ar-S-CH_3 groups, non ionic in nature [13,17]. The exposed polymer thin film lost its ionic character, became less polar and was found to be insoluble in polar solvents. Unexposed regions of the resist film readily dissolved in optimized TMAH solution, controlled by DI-water developer whereas the exposed regions (patterns) were maintained after dipping the exposed resist film in developer which acts as negative tone resist. This has been independently confirmed by EUV photodynamic studies at the Brazilian Synchrotron Light Source (LNLS) Campinas[17]. The Planar Grating Monochromator (PGM), beam line for EUV and soft X-ray spectroscopy (100-1500 eV) which gives a spectral resolution $(E/\Delta E) = 25000$, was used as the monochromatic photon source. The fragmentation products were characterized *in situ* by a QMS mass spectrometer. Additionally, analysis of the thin films after flood exposure was conducted by XPS and NEXAFS. The results obtained at 103.5eV of excitation energy showed efficient photo degradation of the MAPDST homopolymer. Affected mainly were the triflate group but also the carbon backbone of the polymers, but the -SCH_3 group bonded to the phenyl group was resistant, in agreement with previous studies referred to above[13]. SO_2, SO and CF_3 fragments were observed by RGA QMS analysis. Important changes in the surface chemistry were also evidenced with loss of CF_3 and ester groups. The copolymer was more resistant to irradiation than the homopolymer. There was a lower level of out-gassing, but analogous changes were observed such as the retention of the -SCH_3 bonded group and evolution of CF_3 species. These can be explained based on the micro-structural differences between the two resists. The copolymer has 25% MMA groups randomly dispersed in the polymer backbone chain and would not contribute to production of CF_3, SO_2, SO during exposure. In fact the MMA groups would provide stability and function as dissolution inhibitors for EUVL. This study indicates that a modulation of the EUV exposure characteristics of the base MAPDST homopolymer resist can be successfully used to design microstructures providing a fine balance for the RLS, ITRS requirements. The details of these studies will be provided in a subsequent report. [17]

3.1 Resist Contrast curve using e-beam exposure

The sensitivity curves were determined for both the MAPDST-Copolymer resist and MAPDST-Homopolymer resist thin films. For contrast curve, resist polymers films were exposed using e-beam system at 20 KeV for doses 1, 2, 3, ----------10, 20, 30------70 μC/cm^2 for 20 × 100 μm (pad area). After exposure, samples were developed in TMAH-1 developer for 25.6 s by dipping the films in DI-water. The remaining thickness of the MAPDST-MMA copolymer and MAPDST homopolymer in the exposed portion were measured as a function of the exposure dose. After optimized development, normalized remaining thin film thickness (NRT) curves showed they were typical of negative type resists, i.e. the irradiation region of copolymer underwent a polarity change and became effectively insoluble in TMAH based DI-water pH maintained around 12). Thicknesses of developed patterns were measured on Stylus profilometer. Although, this has been termed as a "negative resist", yet its exposure and development characteristics are very similar to those of CA resists. Both the MAPDST-copolymer and MAPDST-homopolymer resists show high contrast (γ) /sensitivity (μC/cm^2) -1.8/2.06 and 3.6/5.25 respectively. These are highly improved when compared with the lit. values of non chemically amplified resists such as AR-N7500,[18] maN2400,[19] HSQ, [20] Fullerol, [21] against the e-beam dose.



(a) MAPDST–MMA Copolymer **(b) MAPDST–Homopolymer**

Figure 2. Sensitivity to electron dose characteristics for (a) MAPDST –homopolymer and (b) MAPDST-MMA copolymer

3.2 20 nm lines pattern using e-beam lithography

We have observed that these n-CARs are sensitive to e-beam irradiation and consequently are anticipated to be applicable for EUVL down to the 16 nm node and below. High resolution patterning of designed MAPDST-homopolymer and MAPDST-MMA copolymer resists were carried out for 20 nm lines patterns using 20 KeV e-beam lithography and exposed for various doses and the process optimized for sub 20 nm lines patterns. Figure 3 shows the 20 nm lines patterns of the MAPDST-homopolymer and MAPDST-MMA copolymer resists at a dose of 40 μC/cm^2 exposed at 20 keV. HRSEM images of isolated 20 nm lines patterns were captured at 77KX magnification whereas the 20 nm L/2S patterns at 25KX. HRSEM images of these non chemical amplified resist were taken after gold deposition of around 5 to 7 nm thick. The 20 nm lines patterns of both the designed resists polymers are very clear and sharp at the edges. Hence, these materials offer a path forward for designing non chemically amplified resist (n-CARs) that may attain higher resolutions than current chemically amplified resists at competitive sensitivities. From these preliminary, EBL experiments, it is now clear that these materials should also work in EUV radiation for 20 nm lines pattern.

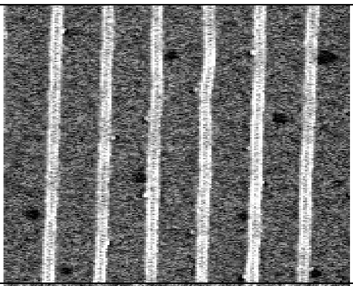
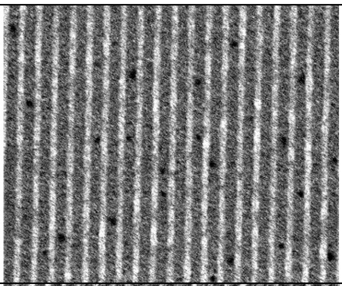
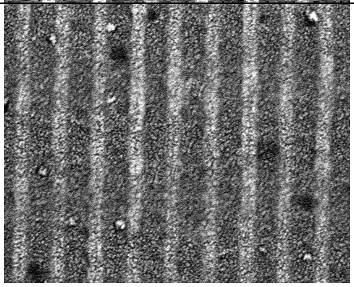
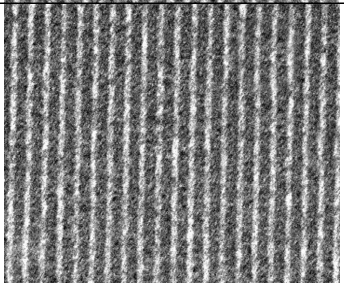
Resist	20 nm Isolated lines pattern at dose 40 μC/cm^2	20 nm with L/2S lines patterns 40 μC/cm^2
MAPDST- Homopolymer		
MAPDST-MMA Copolymer		

Figure 3. SEM images of 20 nm lines patters of negative non chemical amplified resists MAPSDT-homopolymer and MAPDST-MMA copolymer resist pattern with E-Beam direct writing at Dose of 40 μC/cm^2.

3.3 High resolution lines pattern using EUV lithography

Figure 4 summarizes the EUV exposure results of designed non chemical amplified MAPDST-homopolymer and MAPDST-MMA copolymer resists at SEMATECH-Berkeley MET lab. High resolution lines patterns with high quality SEM images were obtained for the both the non chemically amplified resist materials having ultra low LER/LWR which meet the ITRS requirements for sub 22 nm technology. Low line edge roughness is clearly shown from higher magnification (160K mag.) SEM images of MAPDST-homopolymer in Figure 4&5. The 25nm lines with L/2S line space pattern of both the resists polymers are very much clear and sharp at the edges hence these materials provide a path forward for designing non chemically amplified resists (n-CARs) that may attain higher resolutions than current chemically amplified resists at competitive sensitivities.

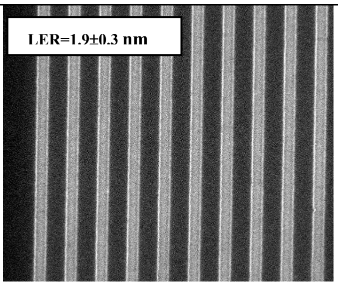
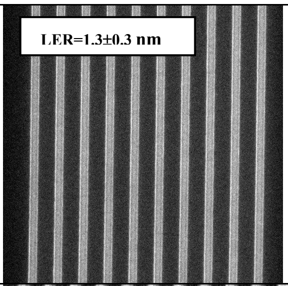
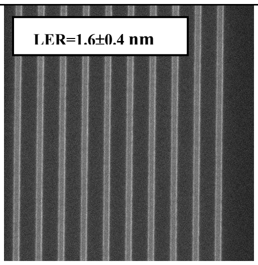
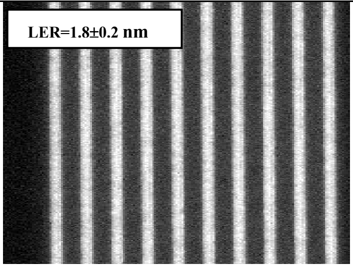
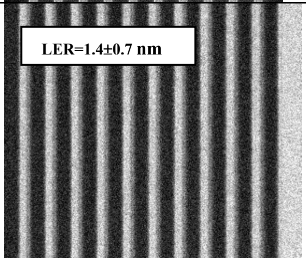
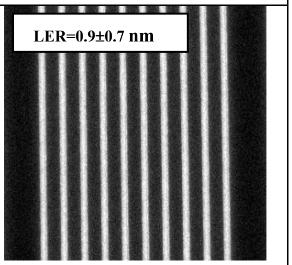
Resist	**40 nm lines with L/2S patterns**	**35nm lines with L/2S patterns**	**25nm lines with L/2S patterns**
MAPDST-Homopolymer			
MAPDST-MMA Copolymer			

Figure 4. EUV exposure results of designed non chemical amplified MAPDST-Homopolymer and MAPDST-MMA copolymer resists at SEMATECH-Berkeley MET lab.

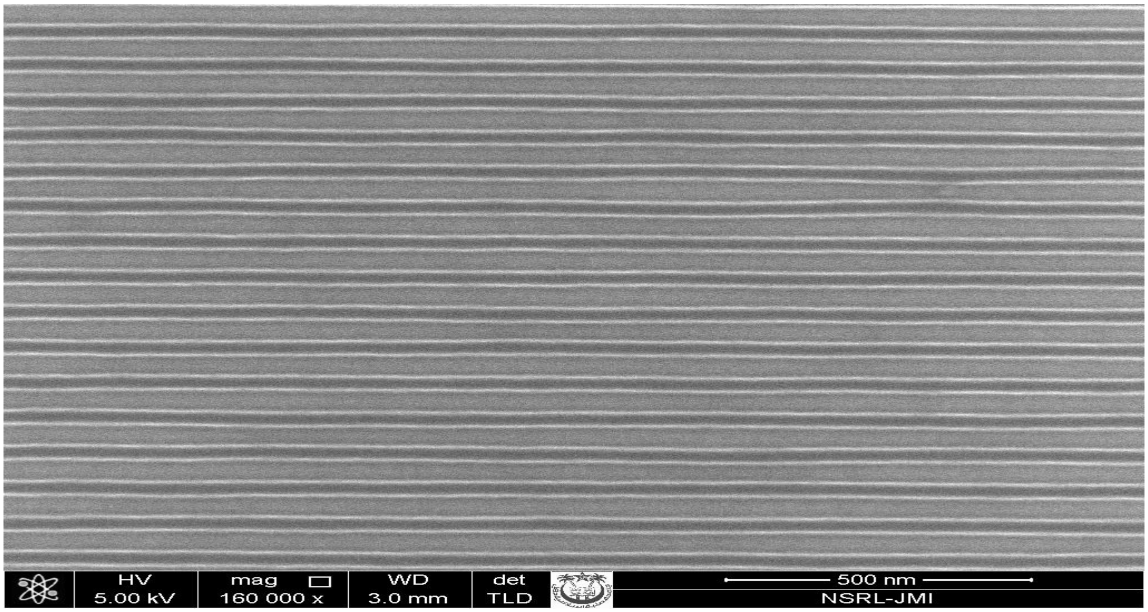


Figure 5. EUV exposure result of 25nm lines with L/2S patterns of designed non chemical amplified MAPDST-Homopolymer resist at SEMATECH-Berkeley MET lab.

3.4 Etch Resistance

The etch chemistry of SF_6 was used to characterize the non chemically amplified MAPDST-homopolymer and MAPDST-MMA copolymer resists. The thickness of the films were measured before and after reactive ion etching (RIE) by Bruker's DektakXT™ Stylus Profilometer. The recipe for plasma etching was SF_6 at a flow rate of 5 sccm at a pressure of 10 mTorr with RF power of 20 W for 20, 30, 40 and 60 seconds for both resist materials. The etch ratios of MAPDST-homopolymer and MAPDST-MMA copolymer resists with respect to the silicon substrate were 7.2:1 and 8.3:1 and are shown in Figure 6 (bar chart). These materials show a very high etch resistance to the silicon substrate when compared to SAL601 and the pure MF07-01 (reported value is 3.1-3.7:1)[22]. MAPDST-MMA copolymer was also tested under etch recipe of CHF_3 /O_2 with a flow rate of 22.5/2.5 sccm at pressure 80 mTorr with RF power of 150 W for 1min. In this case, the etch ratio for MAPDST-MMA copolymer to the silicon dioxide was observed as 0.36:1, which is also comparable to Novolac and PHOST resist polymers (0.40 and 0.33 respectively) under the same conditions. [23]

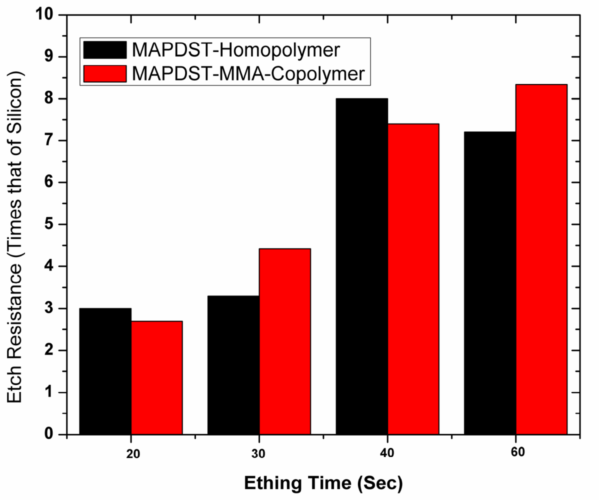


Figure 6. Etch resistance to plasma etching of MAPDST-homopolymer and MAPDST-MMA copolymer resists relative to the etch resistance of silicon.

4. SUMMARY

Further detailed study is necessary to optimize these non chemical amplified resists materials for EUV lithography patterning applications. However, present EUV/EBL results demonstrate their excellent performance characteristics, showing ultra low line edge roughness compared with existing chemical amplified resist materials. Both the designed non chemical amplified MAPDST-copolymer and MAPDST-homopolymer resist show high etch resistance , high contrast. These designed non-chemically amplified resist materials can provide a path forward that may attain higher resolutions for future nanolithography applications.

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