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OPTIMIZATION OF PROCESSING PARAMETERS & METROLOGY FOR NOVEL NCA NEGATIVE RESISTS FOR NGL

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ABSTRACT

It is expected that EUV resists must simultaneously pattern 20-nm half-pitch and below, with an LWR of <1.8 nm, and a sensitivity of 5–20 mJ/cm^2. In order to make a resist perform optimally, new resist chemistry is required. One such approach being investigated by us is the development of polymeric non-CAR negative photo resists for sub 16 nm technology which is directly sensitive to radiation without utilizing the concept of chemical amplification (CARs). These resist designs are accomplished by homopolymers which are prepared from monomers containing sulfonium groups. We have achieved 20 nm patterns by e-beam lithography using this system. Here we will discuss in detail process parameters such as: spinning conditions for film thicknesses <50 nm and resulting surface topographies, baking regimes, exposure conditions and protocols on sensitivity, contrast, resolution and LER/LWR. Etch resistance data on these thin films will also be provided. Our results are aimed to provide a clear understanding of how these critical steps in the lithographic imaging process will affect extendibility of the non-CAR resist concept to sub 20 nanoscale features. Photodynamics and EUV exposure data will be covered.

Keywords: *EBL, EUVL, non-Chemical Amplified Resist, PEB, PAB, Surface roughness, Contrast, Sensitivity and Etch resistance*

1. INTRODUCTION

Development of photoresist materials for extreme ultraviolet lithography (EUVL) technology is one of the major challenges. In addition to answering the well known challenges presented by EUV radiation like the high absorption coefficients, sensitivity, resolution, LER and etch resistance, the demands of high-volume production have to be met. Non-Chemically amplified (non-CAR) resists are anticipated to be strong candidates for nano-fabrication as per the ITRS-2011 road map.[1-6] The main focus of this paper is on the development of EUV & EBL, non chemically amplified resists and ancillary materials for next generation technology, essentially for sub-20-nm half-pitch patterning. Moreover, the sub-20 nm resist pattering is greatly influenced by the resist preparation, spin coating and exposure steps, the temperature treatments (pre bake, post bake and development conditions).[7] These will play a serious role for resist exposure characteristics (contrast and sensitivity), resolution and uniformity (regularity, shape, LER, surface roughness) of the final line patterns.[7-9] In this paper, we investigated the novel non chemically amplified MAPDST-homopolymer negative resist, viscosity, film thickness, spinning speed, effect of the pre bake and post bake temperatures, etch resistance, exposure dose, photodynamic study, surface topography and morphology. These results provide a clearer understanding of how these critical steps in the lithographic imaging process will affect extendibility of the non-CA resist concept to sub 20nm features as per ITRS-2011 road map.

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2. MATERIALS AND METHODS

2.1 Materials

Poly(4-(Methacryloyloxy)phenyl) dimethylsulfonium triflate (MAPDST) homopolymer was synthesized by reacting the monomer r(4-(methacryloyloxy)phenyl)dimethyl sulfonium triflate) (MAPDST) with AIBN (azobisisobutryronitrile) initiator, 1 wt% relative to the monomer in acetonitrile at 60 °C under highly pure nitrogen atmosphere for 2 days.[10-12] The structure of the non chemically amplified MAPDST-homopolymer negative tone resist is shown in Figure 1.

Figure 1. Structure of non-chemically amplified MAPDST-homopolymer negative tone resist

2.2 Thin Film Preparation for EBL Evaluation

The resist solution of the synthesized MAPDST homopolymer was prepared in methanol at 3% by weight of polymer and filtered through a 0.2 µm Teflon filter to remove particles. For e-ebeam evaluation, the thin films of the MAPDST homopolymer negative photoresist solutions were spin coated directly on RCA cleaned bared Si wafers to ~ 30-60 nm thickness and then baked on a hot plate to remove any excess solvent. Resist coated wafer pieces were pre-exposure baked (PEB) at 100ºC for 90 s. 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 our optimized aqueous solutions of TMAH in DI water maintained pH ~ 12 at room temp, rinsed in de-ionized water for about 18 s and blow dried with pure nitrogen gas.

2.3 Film preparations for EUV photodynamic study

Samples were prepared by spin coating the resist solution on cleaned Silicon wafers (0.5 x 1 cm) for desired thickness in a glove box with continuous nitrogen gas (purity grade: 5.0) and red light. Resist coated samples were set in a computer controlled XYZ manipulator by the adhesion of carbon double side tape for the support, inside the glove box with N_2 atmosphere & yellow light. The samples were transported to the UHV chamber inside a closed glove bag under positive flux of nitrogen. Resist films were irradiated at different energies from 103.5 eV (F1s) in UHV conditions (P ~1 x 10^{-9} mbar) for irradiation times 1 and 5 min. Resist films were characterized by X-ray photoelectron spectroscopy (XPS) and Near Edge X-ray Absorption Fine Structure (NEXAFS). X-Ray photoelectron spectroscopy (XPS) data were obtained using a high performance hemispheric SPECSLAB II (Phoibos-Hs 3500 150 analyzer, SPECS) energy analyzer. Near-edge X-ray absorption fine structure (NEXAFS) spectra were obtained by measuring the total electron yield (electron current at the sample) simultaneously with a photon flux monitor (Au grid). Additionally, a quadrupole mass spectrometer (QMS) was

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integrated into the vacuum chamber in order to examine the volatile defragmentation products ablated from the irradiated polymer surface by an in situ gas analysis.

3. RESULTS AND DISCUSSION

3.1 E-Beam evaluation and Post bake condition

High resolution patterning of designed non chemically amplified MAPDST homopolymer negative tone resist was carried out using Raith-150 e-beam lithography system at energy of 20 KeV. After the exposure, samples were developed in TMAH based developer solution. Unexposed MAPDST homopolymer was polar due to its ionic character and therefore soluble in polar solvents such as water. Unexposed regions of the MAPDST homopolymer negative tone resist film readily dissolved in an aqueous TMAH developer (pH 11.5), while the exposed patterns were maintained after dipping the exposed resist film in developer. These are characteristics of a non chemically amplified negative polymeric resist. The MAPDST, homopolymer exhibited 20 nm patterns at a dose of 20, 25 & 40 μC/cm^2 at various post bake conditions were taken at 20KX magnification as given in Table 1. It is evident that at a lower post bake (100 °C/ 90s), 20 nm lines patterns are blurred. Most of the 20 nm lines patterns are getting "sponged down" in developer while at higher dose (40 μC/cm^2), a significant number of the line pattern signature are present. As the post bake temperature increased as shown in the table below, 20 nm line pattern features were clearly demonstrated. Finally, after extensive investigation and gradual optimization of post bake effect onto the exposed resist, a protocol was developed for the high quality 20 nm lines pattern of MAPDST homopolymer at 115°C/90s as per sub 20nm technology node.

Table 1. E-Beam lithography results, 20 nm features, target for Non chemically amplified (MAPDST-homopolymer) negative resist under different post bake condition

Post Bake Annealing (°C)	**Exposure dose (20 nm Lines patterns)**		
	20 μC/cm^2	25 μC/cm^2	40 μC/cm^2
100			
110			
115			

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3.2 Contrast Analysis

The contrast curve, of MAPDST homopolymer resist films were determined after the exposure of e-beam on a Raith-150 system for varying doses 1, 2, 3, ----------9,10, 20, 30------70 µC/cm^2 for 20 × 100 µm pads at 20 KeV. After exposure, the resist was developed for various developing times (25, 21 and 17 sec) through the dip of exposed films in DI-water with pH ~ 11.5-12, adjusted by 0.26 N TMAH as shown in Figure 2. The thickness of developed patterns were measured on Stylus profilometer. We obtained a high contrast of 3.6 with sensitivity 5.25 µC/cm^2 for developing in 17 sec. It is clearly shown in Figure 1that contrast of the MAPDST-homopolymer is highly dependent on developing conditions.

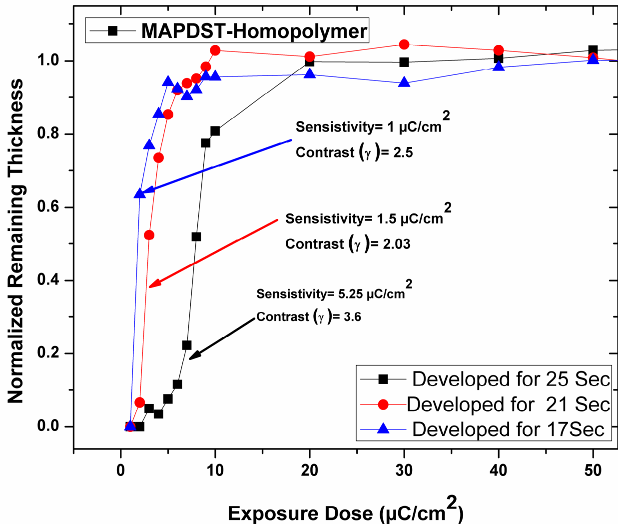

Figure 2. NRT response curves of Non chemically amplified Resist (MAPDST-homopolymer) processed for different development times while keeping other conditions the same i. e. PEB, PAB and exposure condition.

3.3 Surface roughness Developed Film

The surface roughness of MAPDST homopolymer after e-beam exposure for various doses and developed in TMAH based developer as stated above is shown in Figure 3(a&b). The RMS values (AFM analysis) of MAPDST homopolymer surface varies with E-beam lithography exposure dose. It is clearly shown in the Figure 3(a) that roughness remains constant till 25 µC/cm^2, below this critical dose, it increases rapidly. It appears that optimum dose window for lesser LER and LWR as per next generation lithography demand is 25-60 µC/cm^2.

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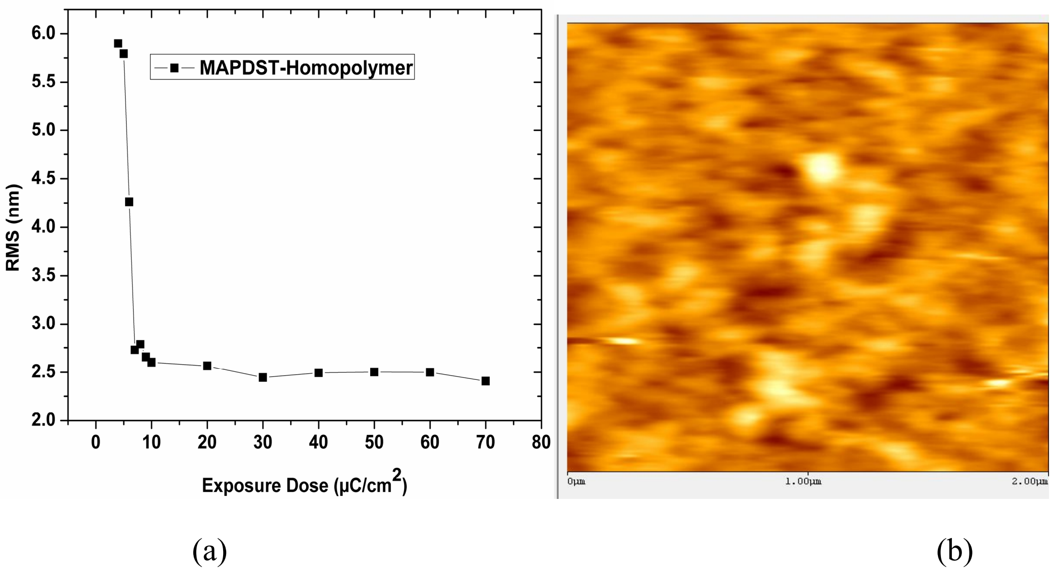

(a) (b)

Figure 3. (a) Surface roughness (rms value) of MAPDST-Homopolymer with E-beam exposure dose under same condition i.e. PEB/PAB and same developing condition and (b) AFM image of MAPDST-homopolymer patterned at dose of 9 $\mu C/cm^2$.

3.4 EUV photodynamic study

To meet the resolution requirements for next generation node technology, 13.5 nm (98.5 eV) has emerged as potential excitation energy. The excitation energy of 103.5 eV is close to 98.5 eV and due to its high intensity in the PGM beam line; it was selected to test the effect of the EUV radiation on the MAPDST homopolymer films. XPS spectroscopy was used to prove the surface chemical changes after irradiation. Survey XPS spectra of pristine and irradiated MAPDST homopolymer films showed a continuous decrease in the F1s, O1s and S2p signal with an increase in the C1s signal with the increase in the irradiation time. The changes in the surface chemistry with the irradiation time can be clearly observed in the HR-XPS spectra of C1s and S2p envelope as depicted in Figure 4. NEXAFS (Near-edge X-ray absorption fine structure) and QMS (quadrupole mass spectrometer) techniques also confirmed the low stability of the triflate group compared to the polymer backbone. The details of these results including NEXAFS analysis will be provided in a subsequent report.[13] The main assessment from these studies is that on EUV exposures, the triflate counter ion is susceptible to immediate degradation, while the sulfur-methyl bond is fairly resistant. This would indicate that an Ar-S-CH_3 results that is nonionic and hence not soluble in developer.

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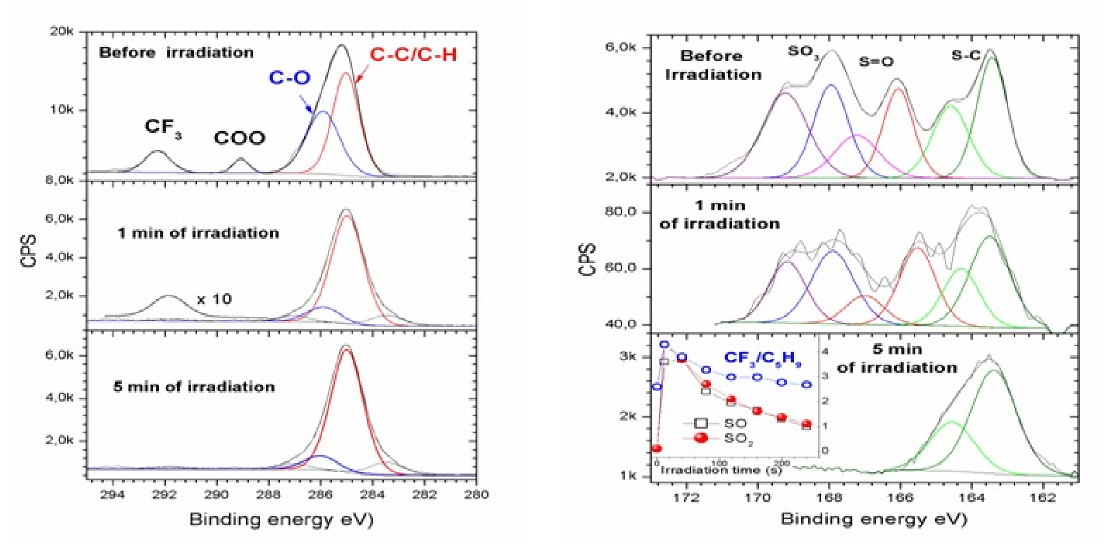

Figure 4. High-resolution XPS spectra of the C 1s (left) and S 2p (right) envelope of the MAPDST homopolymer films before irradiation and after 1 and 5 min of SR irradiation at 103.5 eV.

3.5 EUV Lithography evaluation for High resolution lines pattern

For EUV evaluation, the MAPDST homopolymer negative tone resist solution was prepared in methanol and filtered by 0.2 micron Teflon filter and spin-coated onto HMDS treated 200 mm silicon wafer for ~ 40 nm thin films. The thin films of MAPDST-homopolymer were prebaked at 100 °C for 90 sec. First the E0 center dose was calculated from test wafer for MAPDST-Homopolymer to be around 30 $mJcm^{-2}$, but the actual value of E_0 of MAPDST-homopolymer is not certain at this time. It is highly dependent on the developer conditions, and more test runs are required for EUV optimizations. The resulting photo resist layers were flood exposed with the respective E_0 array using mask IMO228775 with Field of R_4C_3 at SEMATECH Berkeley Microfield Exposure Tool (MET). The sample was post exposed baked at 115 °C for 90 sec and developed with our optimized TMAH based developer named as TMAH-1 developer to obtained high resolution lines patterns. Figure 5 shows high resolution 40, 30 and 25 nm lines with L/2S line space patterns of non chemical amplified MAPDST-homopolymer negative resist where it can be clearly seen that 25 nm lines patterns are well-resolved and having ultra low 1.6 nm line edge roughness. This result clearly establishes MAPDST-homopolymer as a cutting-edge high resolution resist capable of resolving sub 25 nm hp having ultra low LER/LWR which meet the ITRS requirements for sub 22 nm technology. High resolution is limited by line collapse and therefore, several studies, such as developing conditions, profile control and additional process optimizations are currently ongoing.

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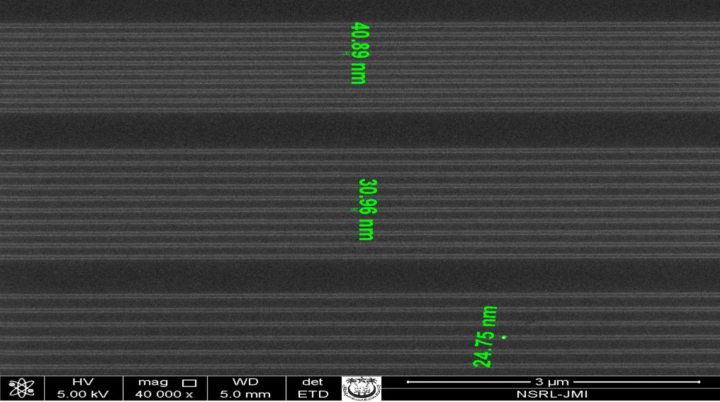

Figure 5. Top-view SEM image of 40, 30 and 25 nm lines with L/2S line space patterns of non chemically amplified MAPDST-homopolymer negative resist under EUV exposure.

3.6 Etch Resistance

STRIE-320PC system was used for etch resistance investigation of MAPDST-homopolymer. The etch study of this resist was done in SF_6 chemistry, and the thickness were measured before and after reactive ion etching (RIE) by Bruker's DektakXT™ Stylus Profilometer, which has the Key Features: 2.0 µm diamond-tip stylus. The etchant recipe was SF_6 at a flow rate of 5 sccm at pressure of 10 mTorr with RF power of 20 W for 20, 30, 40 and 60 seconds. The etch ratio of MAPDST-homopolymer to the silicon substrate was 7.2:1 are shown in Figure 6 (bar chart). These etch ratio values clearly indicate the higher etch resistance compared to polymers SAL601 and the pure MF07-01 (reported value is 3.1-3.7:1).[14]

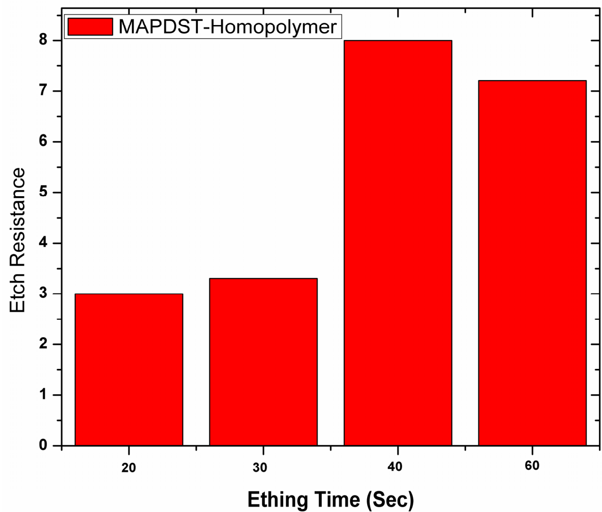

Figure 6. Etch resistance to plasma etching of MAPDST-homopolymer resist relative to the etch resistance of silicon.

4. CONCLUSIONS

The EBL, EUVL and photodynamics investigations of the novel resist, MAPDST homopolymer demonstrated its high performance capabilities with higher contrast ratio and etch resistance and asserted itself as a potential

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viable candidate for next generation lithography applications. However, additional work is underway to investigate a viable resist for the target set by the International Technology Roadmap for Semiconductors (ITRS).

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