

Towards novel non-chemically amplified (n-CARS) negative resists for electron beam lithography applications†

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A novel, non-chemically amplified negative resist was synthesized and characterized for next generation lithography applications. This resist material was shown to be directly sensitive to radiation without utilizing the concept of chemical amplification (CAR) and resulted in high-resolution 20 nm features. This resist design is accomplished by copolymers that are prepared from a monomer containing a sulfonium group which is sensitive to e-beam irradiation. Under 20 keV e-beam imaging and TMAH development, a sensitivity of $2.06 \mu\text{C cm}^{-2}$ and contrast of 1.8 were obtained. It has an LER of 20 nm, 10 line pattern varies from 1.8 ± 0.3 to 2.3 ± 0.4 nm.

In recent times, the semiconductor industry has progressed remarkably with the development of integrated circuit (IC) technology that solely depends on research effort in various high resolution lithography techniques including DUV, EUV, electron beam and X-ray lithography technologies, sensitive resist materials systems and appropriate thin film deposition methods. According to ITRS-2011, extreme ultraviolet lithography (EUVL) at 13.5 nm is one of the most likely post-optical techniques to pattern sub 20 nm half-pitch photoresists for high-volume IC chip manufacturing.¹ Beside the issues associated with the availability of extreme ultraviolet (EUV) power sources and masks, the most prominent challenge for promoting EUVL is the requirement for improvements in resist performance. However, the major key challenges that remain to be resolved to meet the demands of high-volume production include development of photoresists capable of concurrently meeting industry requirements for resolution, sensitivity, and line edge roughness (LER).^{1,2}

Since the introduction of chemically amplified resists (CARs), they have enabled technology to reduce the half-pitch of patterned structures to 22 nm in production. However, chemically amplified resists can limit the ultimate minimum half pitch resolution due to acid diffusion problems, low sensitivity and post exposure instability.² In addition to these effects, line edge roughness (LER) or line width roughness (LWR) have become critical for sub 20 nm technology that must be controlled, and this places an additional constraint on the chemically amplified resist (CAR).^{3,4} For chemically amplified resists, the contest between sensitivity, resolution, and LWR has been called the 'triangle of death' for sub 20 nm technology.^{5,6} However, these problems are mainly associated with chemically amplified positive tone resist materials. Recently, attention has focused on the development of non-chemically amplified resists (non-CARs) for future lithography nodes. One such approach that we are investigating is the development of non-chemically amplified (n-CAR) negative resists based on polymeric material for sub 16 nm technology that will overcome all the drawbacks of CARs and be complementary to current chip fabrication. In addition to maintaining tolerable levels of LER, successful non-CAR thin film materials must demonstrate high sensitivity, resolution and plasma etch resistance. Although novel non-CAR materials have demonstrated resolutions below 20 nm, their application remains limited due to sensitivities and several other issues.⁷ A negative-tone molecular glass that was recently reported based on a cationic polymerization mechanism, was evaluated using e-beam/EUV and developed in organic solvent.⁸ Similarly, a polyphenol molecular glass and azide cross-linker also showed good resolution and reduced LER.^{9,10} Although partial resolution of a 14 nm half-pitch has been recently demonstrated using chemically amplified resists (CARs), the dose of 30 mJ cm^{-2} is still far short of the target of 5–20 mJ cm^{-2} .^{11–15} A negative-tone inorganic resist, hydrogen silsesquioxane (HSQ), has a resolution below 10 nm at 100 keV with a base dose of 33 mC cm^{-2} ,¹⁶ resolves patterns with half-pitches as small as 20 nm with EUV interference lithography,¹⁷ and has less than 2 nm LER.^{18,19} More recently, the Robinson group

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developed a fullerene based chemically amplified e-beam resist and reported good sensitivity, resolution, LWR ~ 4 nm and higher etch resistance comparable to the commercially available SAL601 resist.^{20–23} While comparing the performances of the reported efficient resists, we found that our newly developed resist possesses improved sensitivity compared to some of the reported values (Table S2, ESI†). New inorganic resists with Zr and Hf for e-beam lithography have demonstrated, using a 30 keV electron-beam,^{24,25} sensitivities as low as $8 \mu\text{C cm}^{-2}$, achieved 15 nm lines and 36 nm dense features at higher doses with approximately 2 nm of LWR. More recently, two more new non-chemically amplified inorganic resists (XE15CB base dose = $735 \mu\text{C cm}^{-2}$ and XE15IB, base dose = $300 \mu\text{C cm}^{-2}$ provided by Inpria) were also investigated.²⁶

In this letter, we discuss the design and synthesis of novel non-chemically amplified negative resists for advanced nano lithography applications and their characterisation by e-beam lithography. As a prelude to EUV lithography, we have carried out the e-beam exposure of novel non-chemically amplified negative resists (n-CARs) to determine their sensitivity and imaging capabilities at the 20 nm node and below. Herein we report our preliminary findings for these resists.

The development of such advanced resists demands materials that are directly sensitive to radiation without utilizing the concept of chemical amplification (CAR). Hence, to increase the sensitivity of a polymer directly towards radiation, a highly radiation sensitive group must be introduced into the polymer units. Sulfonium salts have long been found to be sensitive to UV radiation and e-beam irradiation,^{27–30} therefore these would be useful for EUVL down to the 16 nm node and below.

The monomer (4-(methacryloyloxy)phenyl)dimethylsulfonium triflate (MAPDST) was synthesized following a procedure reported in the literature.³¹ A MAPDST–MMA copolymer was synthesized by reacting MAPDST and methyl methacrylate (MMA) in an equal molar ratio in the presence of an AIBN (azobisisobutyronitrile) initiator (1 wt% relative to both the monomers) in tetrahydrofuran and acetonitrile (80 : 20) at 60°C under a nitrogen atmosphere for 2 days. The synthesized MAPDST–MMA copolymer was obtained as a white crystalline solid and its chemical structure is shown in Fig. 1. The molecular weight M_w of this newly developed copolymer was calculated to be 4300 with a polydispersity of 2.02 at the maximum displacement of the curve by gel permeation chromatography (GPC). The compositions determined by $^1\text{H NMR}$ were 75% MAPDST and 25% MMA. The glass transition temperature (T_g) was determined by DSC and is 165°C .

The solid polymer was then dissolved in methanol to 3% by weight to form a resist solution. The resist solution was filtered through a $0.2 \mu\text{m}$ Teflon filter in order to remove any particles present. Prior to the lithography protocols, $2''$ p-type (100) silicon wafers were cleaned by an RCA cleaning method and dehydration baked for 10 min at 200°C and cooled to room temp. The thin films of copolymer solution were then spin-coated on $2''$ quarter pieces of p-type silicon (100) wafers at 5000 rpm for 60 s to achieve the desired thicknesses. A pre-exposure bake for the resist-coated wafers was performed at 90°C for 120 s on a hot plate to remove solvent from the resist.

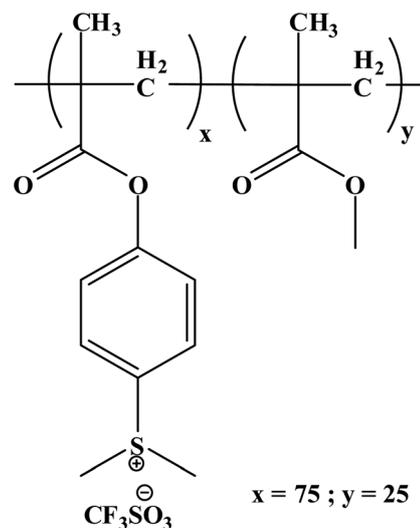


Fig. 1 Chemical structure of the MAPDST–MMA copolymer.

Exposures were carried out using e-beam lithography Raith150 system at an exposure energy of 20 keV with a $20 \mu\text{m}$ aperture and a 196.8 pA beam current by covering a broad range of dose calculation. After exposure, a post exposure bake was performed at 100°C for 120 s on a hot plate. The exposed samples were developed in 0.022 N tetramethyl ammonium hydroxide (TMAH) solution prepared in DI water by maintaining the pH at 11.54 at room temperature for 20 s, rinsed in de-ionized water for about 15 s and blow dried with pure nitrogen gas. The resist thickness was determined using a ZETA 150 optical profiler and found to be 50 nm. The exposed features were evaluated with the SEM function of a Raith 150 system at an energy of 5 keV.

However, for EUVL to achieve a sub 22 nm technology node, a resist thickness of around 50 nm or below becomes critical. This resist thickness will further be reduced with the reduction in feature sizes. Consequently it becomes very important to enhance polymer absorption for the efficient use of incident photons. With the reduction in feature size, pattern collapse is also another serious problem in improving the resist resolution. Etch resistance is another important factor for the development of thin resist materials for the 16 nm node and below. Hence, a polymer having radiation sensitive units is needed to overcome the above mentioned difficulties. To develop such resist materials, we directed our effort to incorporate a radiation sensitive sulfonium moiety as a pendant unit in the polymer backbone (Fig. 1).^{28,29} The motivation for this polymer to act as a resist was based upon a preliminary photochemical study carried out on the polymer.²⁹

High resolution patterning of the above designed copolymer resist was carried out using 20 keV e-beam lithography. Unexposed regions of the resist film readily dissolved in an aqueous TMAH developer while the exposed regions (patterns) were maintained after dipping the exposed resist film in developer. The SEM results of the e-beam patterning of the copolymer resist are shown in Fig. 2 for 20 nm, 1 : 2 line/space, exposed at a dose of $35 \mu\text{C cm}^{-2}$ at 20 keV. The computation of LER

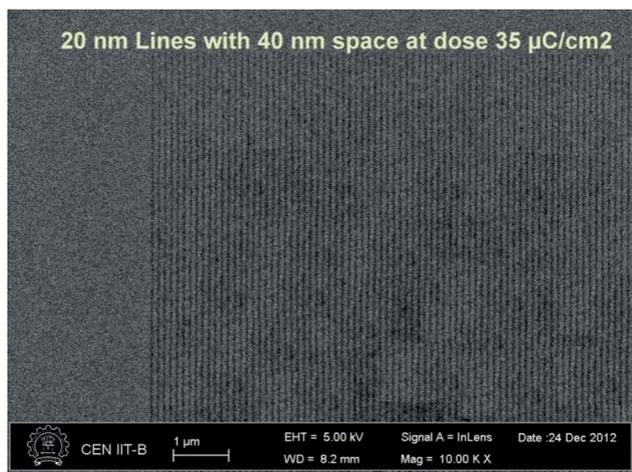


Fig. 2 SEM results of the e-beam patterning of the negative tone copolymer resist for 20 nm 1 : 2 line/space, patterns exposed at a dose of $35 \mu\text{C cm}^{-2}$ at 20 keV.

($\sim 1.8 \pm 0.3$ to 2.3 ± 0.4 nm) was carried out from the same dense pattern in Fig. 2. The high-resolution SEM image at $77\text{K}\times$, as shown in Fig. 3 of the e-beam patterning of the copolymer resist, was acquired after a $\sim 5\text{--}7$ nm gold thin film was sputtered onto the sample surface to minimize the charging due to deflected secondary electrons and secondary electron emission from the e-beam patterned resist surface. The magnified resist pattern for 20 nm line patterns with a 100 nm space, exposed at a dose of $40 \mu\text{C cm}^{-2}$ at 20 keV is shown in Fig. 3. Due to its ionic character, the unexposed polymer was polar in nature, and was therefore 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 S–C bonds in the sulfonium groups were cleaved.²⁵ The irradiated polymer

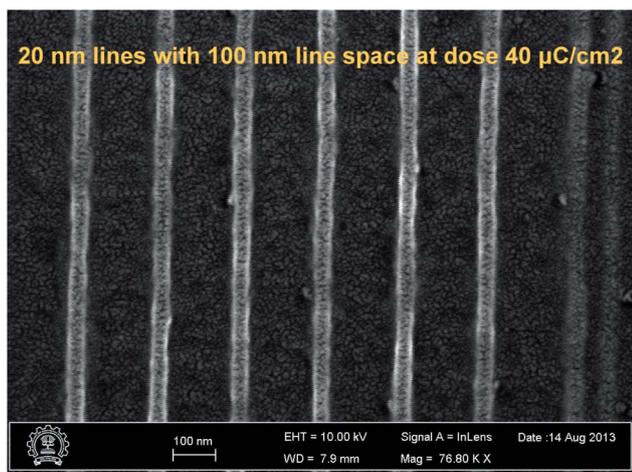


Fig. 3 SEM results of the e-beam patterning of the negative tone copolymer resist for isolated 20 nm line patterns with 100 nm space, patterns exposed at a dose of $40 \mu\text{C cm}^{-2}$.

lost its ionic character, became less polar and was found to be insoluble in polar solvents. Thus HRSEM patterns of the “negative tone” obtained for this resist by exposure to 20 keV e-beam lithography systems revealed fine features. The HRSEM image of the negative tone lines were obtained at a dose of $40 \mu\text{C cm}^{-2}$ and were found to be clear and highly resolved. The LERs of 20 nm line patterns were calculated by SuMMIT® software and it varied from 1.8 ± 0.3 to 2.3 ± 0.4 nm.

The quality of resist materials is generally characterized by their contrast curves. The sensitivity curve was measured for the MAPDST copolymer resist thin films. The residual thickness of the MAPDST copolymer in the exposed portion was measured as a function of the exposure dose. That the present copolymer acts as negative type resist was confirmed from the results of the normalized thin film thickness that was observed to increase with increasing exposure dose. These experimental results indicate that the irradiation region of the copolymer underwent a polarity change and became effectively insoluble in 0.022 N TMAH developer prepared in DI-water (pH = 11.54) whereas unexposed regions of the resist film readily dissolved in TMAH developer solution.

Fig. 4 shows a contrast curve for the MAPDST copolymer resist, which plots the relative film thickness as a function of the e-beam dose, following a post-exposure bake step at 100°C and development in 0.022 N TMAH developer solutions. The contrast curve of the n-CAR illustrates what the ITRS roadmap for the future technology nodes requires: a high resist sensitivity¹ of $5\text{--}30 \mu\text{C cm}^{-2}$ and high contrast. The MAPDST copolymer exhibits a contrast of $\gamma = 1.8$ with a sensitivity of $2.06 \mu\text{C cm}^{-2}$. The sensitivity of the resist is far superior to that of HSQ (base dose = $770 \mu\text{C cm}^{-2}$ with 25% TMAH).

After exposure and development, the etch resistance data were obtained on STRIE tool under two recipes. The first etch recipe involved SF_6 with a flow rate of 5 sccm at a pressure of 10 mTorr with an RF power of 20 W for 1 min. The etch ratio of the MAPDST-copolymer to the silicon substrate was found to be

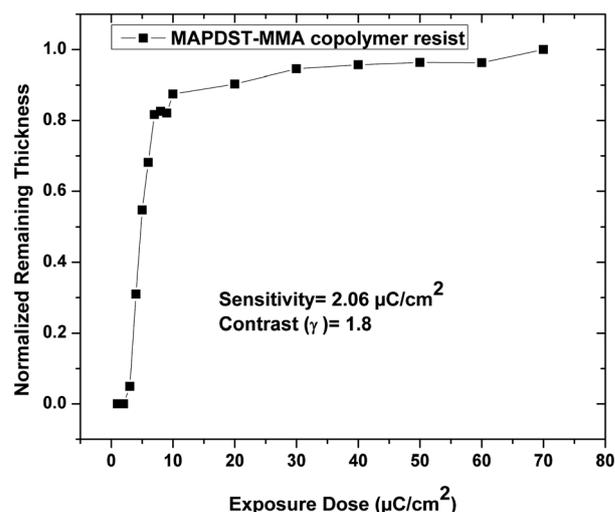


Fig. 4 Sensitivity to e-beam dose characteristics of the MAPDST-MMA copolymer.

8.34 : 1. This etch ratio value clearly indicated a higher etch resistance compared to that of polymers SAL601 and the pure MF07-01 (reported value is 3.1–3.7 : 1).²¹ The second recipe involved CHF_3/O_2 with a flow rate of 22.5/2.5 sccm at a pressure of 80 mTorr with an RF power of 150 W for 1 min. In this case, the etch ratio for the MAPDST-copolymer to silicon dioxide was observed to be 0.36 : 1, which is also comparable to Novolac and PHOST resist polymers (0.40 and 0.33 respectively) under the same conditions.³²

Conclusions

Taking advantage of the high sensitivity of the sulfonium group towards electron beam radiation, a novel MAPDST–MMA copolymer containing this sensitive group has been developed as a non-chemical amplified negative resist for advanced nano lithography applications. This new material was found to be extremely sensitive to e-beam radiation and therefore resulted in high-resolution 20 nm features. Using this non-chemically amplified negative resist, the MAPDST–MMA copolymer, we could obtain an excellent resolution of 20 nm 1 : 2 line/space with low LERs from 1.8 ± 0.3 to 2.3 ± 0.4 nm. This resist material also showed good etch resistance against plasma etch chemistry. These experimental results strongly support the potential of the MAPDST–MMA copolymer as a highly efficient, non-chemically amplified negative resist. Furthermore, they could be promising candidates for future generation high resolution e-beam and EUV patterning materials due to their favourable combination of resolution, sensitivity, and line edge roughness. We are currently conducting EUV exposures of the resist. Results will be reported subsequently in the near future.

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