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Polyarylenesulfonium Salt as a Novel and Versatile Nonchemically Amplified Negative Tone Photoresist for High-Resolution Extreme Ultraviolet Lithography Applications

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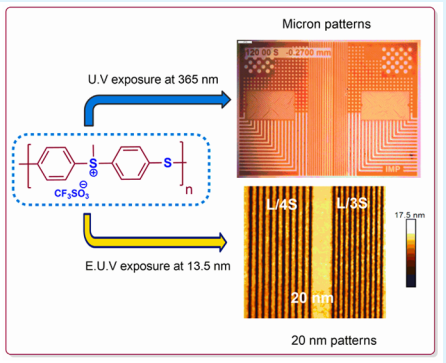
Supporting Information

ABSTRACT: The present report demonstrates the potential of a polyarylenesulfonium polymer, poly[methyl(4-(phenylthio)-phenyl)-sulfoniumtrifluoromethanesulfonate] (PAS), as a versatile nonchemically amplified negative tone photoresist for next-generation lithography (NGL) applications starting from i-line ($\lambda \sim 365$ nm) to extreme ultraviolet (EUV, $\lambda \sim 13.5$ nm) lithography. PAS exhibited considerable contrast (γ), 0.08, toward EUV and patterned 20 nm features successfully.



KEYWORDS: *polyarylenesulfonium salts, EUV lithography (13.5 nm), i-line (365 nm), 20 nm line patterns, complex features*

Development of novel photoresist materials for high-resolution lithography applications is an important but extremely challenging task. According to the International Technology Roadmap for Semiconductors (ITRS-2015),[1,2] the microelectronics industry is projected to pattern integrated circuits at sub-20 nm resolution in the near future. However, traditionally used chemically amplified resists (CARs) that depend on blended or polymer-bound photoacid generators (PAGs)[3,4] for achieving solubility differentiation are often associated with inherent problems such as high line edge roughness (LER), line width roughness (LWR), low sensitivity, post exposure instability, and process complexity for high-resolution patterning applications.[5−7] Therefore, increased attention is now being focused on the development of novel nonchemically amplified resists (n-CARs) to meet the targets set by ITRS-2015. n-CARs are materials that are directly sensitive to radiation and do not require PAGs in their formulation.[8,9] In this context, a wide range of novel organic, inorganic, organometallic, and hybrid resists have been developed in recent years for high-resolution lithography applications.[10−17] Nevertheless, the number of organic polymer based n-CARs is highly limited compared to the number of CARs reported to date. Therefore, the development of high-end organic polymer-based n-CARs with strong lithographic potentials is highly important, especially for sub-20 nm patterning applications with low LER/LWR features.

Poly[methyl(4-(phenylthio)-phenyl)-sulfoniumtrifluoromethanesulfonate] (PAS) derivatives have been investigated for their photochemical behaviors.[18,19] However, their potential as photoresists for multiple lithography applications has not yet been realized. Herein, we report the versatile lithographic performances of polyarylenesulfonium salts as a new class of n-CARs for micro- and nanopatterning applications using a representative member of this family, PAS (Figure 1). PAS is a soluble photoactive polymer with a regular

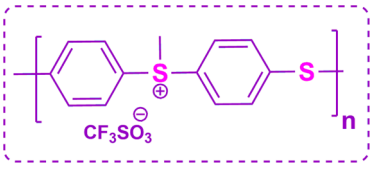


Figure 1. Chemical structure of PAS resist.

structure of alternating thiophenylene and phenyl alkyl sulfonium units. PAS is generally synthesized by sulfoxide-acid reaction.[18,20] Previous studies have shown that the irradiation of PAS with $\lambda \sim 365$ nm results in selective photolysis of its chain generating methyl(4-(phenylthio)-phenyl)sulfane fragments.[18] Based upon the photodegradation behaviors of PAS, we envisaged its use in micron ($\lambda \sim 365$ nm,

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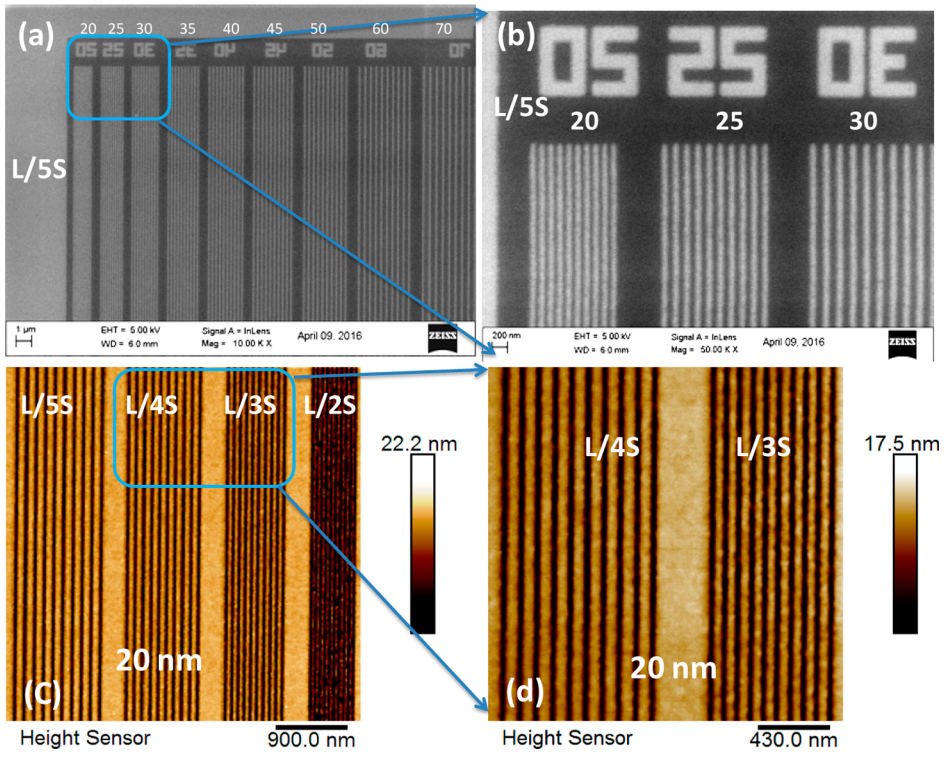

Figure 2. (a) FE-SEM image of isolated patterns of 20, 25, 30, 35, 40, 45, 50, 60, and 70 nm with L/5S (line/space) gap; (b) high-magnification image of 20, 25, and 30 nm isolated lines with L/5S; (c) AFM image of 20 nm line patterns with L/2S to L/5S; and (d) high-resolution AFM image of 20 nm line patterns with L/4S and L/3S, CD on the mask.

i-line) and nanoscale ($\lambda \sim 13.5$ nm, EUV) photolithography applications. The pattering processes employed herein followed the standard semiconductor fabrication procedures, and the present study revealed the capability of PAS to act as negative and positive tone n-CAR resists for next-generation lithography (NGL) applications.

A brown colored solid of PAS (see Figure 1) was synthesized by using a reported procedure[18,20] (see Supporting Information for synthesis and characterization details). The weight-average molecular weight of PAS was calculated as 5675 g/mol with a polydispersity index (PDI) of 1.3 by GPC analysis using a mixed-B column (see Supporting Information for details). Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to investigate the thermal stability, glass transition temperature, and melting temperature of PAS. TGA studies revealed that PAS is thermally stable up to 190 °C. The glass transition and melting temperatures of PAS were found to be 76−80 and 132 °C, respectively. These studies revealed the adequate thermal properties of PAS for lithography applications (see Figure S14 and S15, Supporting Information).

Preliminary evaluation of PAS as a n-CAR was performed by using an i-line ($\lambda \sim 365$ nm) lithography tool. Resist solution was prepared by dissolving PAS in acetonitrile (2%, w/v) followed by filtration through a 0.2 μm Teflon filter. Hexamethyldisilazane (HMDS) primed p-type Si(100) wafers were used as substrates for resist coating. The resist solution was spin-coated onto the wafer at a speed of 4500 rpm for 60 s followed by prebake at 100 °C for 90 s to get the desired thin films. The surface morphology of the thin films obtained was analyzed by using an optical microscope as well as AFM (see Figure S16 and S17, Supporting Information). The thickness of the resist films was measured as ∼34 nm using a stylus profilometer (Figure S18, Supporting Information). The computed RMS roughness of the films was ∼0.34 nm (Figure S17c, Supporting Information). The resist films were then exposed to i-line ($\lambda \sim 365$ nm) radiation for 120 s using a mask-less lithography exposure tool for micropatterning application. The exposed films were post baked at 50 °C for 60 s and then developed for 30 s with a developer solution of 0.05 N tetrabutylammonium hydroxide (TBAH). We used 0.05 N TBAH solution as the developer for PAS resist as it was observed that the industry standard 0.262 N TMAH developer leads to overdevelopment of the exposed films. The well-resolved patterns obtained by using PAS as a negative tone i-line resist are shown in Figure S19 (Supporting Information). It was observed that the PAS resist can also be used as a positive tone resist by employing an organic developer, 1,4-dioxane, instead of TBAH (see Figure S20, Supporting Information). These preliminary studies therefore revealed that by switching the developer and processing conditions PAS can be used as a dual tone n-CAR for micropatterning applications.

Based on the successful i-line lithography studies on micropatterning, PAS resist was tested as a negative tone n-CAR for high-resolution nanopatterning applications under EUVL conditions as well. Some of the experimental conditions (such as the thin-film preparation, prebake, postbake, and developing conditions) employed for EUVL studies were same as that used for i-line lithography studies. The EUV exposures were performed with a MET microexposure tool available at SEMATECH Berkeley using an industry standard EUV mask—IMO228775 with R4C3 (LBNL low-flarebright-field).[21] The EUV exposed wafers were characterized by using high-resolution FE-SEM and AFM tools. FE-SEM studies showed 20, 25, 30, 35, 40, 45, 50, 60, and 70 nm critical dimension (CD) with well-resolved 1:5 (line/space) patterns (see Figure

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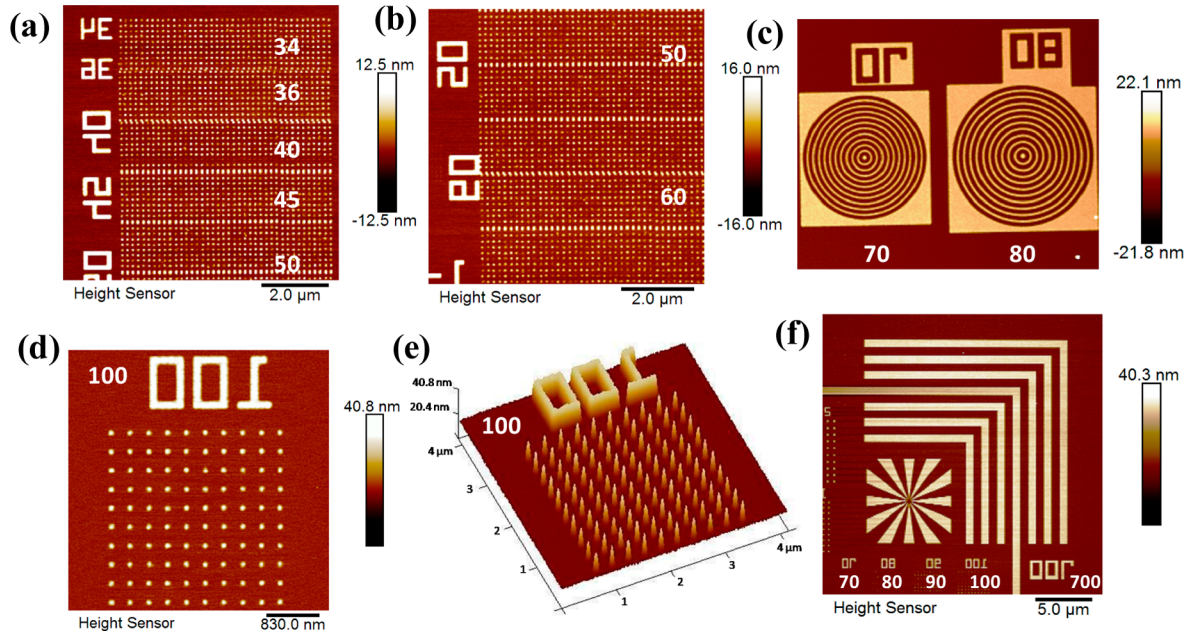

Figure 3. HR-AFM complex features of EUV exposed PAS polymer. (a) Highly dense arrays of 34, 36, 40, and 45 nm dots; (b) 50 and 60 nm dots; (c) circular patterns of PAS with 70 and 80 nm features; (d) 100 nm dots; (e) 3D view of 100 nm dots; (f) an image showing star-elbow features.

2a). The higher-magnification SEM images of 20, 25, and 30 nm features with 1:5 line/space patterns are shown in Figure 2b. HR-AFM images of EUV-exposed PAS resist films showed line patterns up to 20 nm (printed CD on the mask) with 1:3 line/space or with the minimum resolved pitch of ~80 nm as shown in Figure 2c,d. Similarly, 32 nm line patterns with 1:2 to 1:5 line/space features obtained are shown in Figure S21 (Supporting Information). The LER of the 30 nm line patterns of PAS resist (Figure S22, Supporting Information) with 1:4 line/space characteristics was calculated by using standard metrology analysis tools of the "SUMMIT" package as 3.6 ± 0.3 nm. However, due to the poor resolution of the images, the LERs of 20 and 25 nm line patterns with various line/space characteristics could not be measured. The sizing dose in these cases was calculated as ~43.5 mJ/cm^2. The center dose was calculated as 17.6 mJ/cm^2. Thickness measurements performed on the developed line patterns with 20, 25, and 30 nm features showed a thickness of ~26.4 nm, which is less than the original film thickness (~34 nm) measured (see Figure S23, Supporting Information). We assume that this could mainly be due to the metrology artifact called "tip convolution artifact".

Complex nanofeatures such as nanodots, nanopillars, nanorings, and star-elbow features often find special interest in the semiconductor industry because of their applicability in diverse fields.[22−24] PAS is capable of patterning complex nanofeatures including nanodots, nanorings, and star-elbow features under EUVL conditions. HR-AFM images shown in Figure 3a,b reveal dense arrays of nanodots with feature sizes ranging from 34, 36, 40, 45, 50 to 60 nm. Moreover, well-resolved circular patterns with 70 and 80 nm features, 2D and 3D arrays of nanodots with 100 nm features, and the star-elbow complex features achieved with PAS resist are shown in Figure 3(c−f). Some damages were observed on the sufaces of certain features, especially in the case of high-resolution nanodots and 1:2 (L/S) 20 nm line feature (see Figures 3a,b and Figure 2c). We assume that this could be due to the structure loss or line collapse occurring under the given development conditions.

A possible mechanism for the action of PAS resist is given in the Supporting Information, Figure S24. Sulfonium triflates are known to undergo photodegradation upon exposure to high-energy EUV radiation.[8,9,24] The PAS polymer is also known to undergo photodegradation to form methyl(4-(phenylthio)-phenyl)sulfane leading to a polarity change upon irradiation.[18] As a result, the neutral Ar−S−CH_3 moiety is expected to form in the resist film during the postexposure bake and development processes. This renders the irradiated area insoluble in TBAH developer because of the change in polarity from initially hydrophilic to hydrophobic. However, if an organic developer, 1,4-dioxane, is used, the exposed nonpolar regions will get developed, while the unexposed polar regions will remain intact on the wafer. Therefore, PAS can act as a dual-tone photoresist. However, detailed photophysical studies are required to understand the complete mechanism behind the observed lithographic properties of PAS.

A contrast curve for PAS resist was calculated based on the EUV exposure results. The residual thickness of the PAS resist at EUV exposed regions was found to depend on the exposure dose employed. The plot of normalized thickness of the resist film vs the EUV exposure dose is given in Figure 4. These studies showed that the normalized film thickness of PAS resist increases gradually with an increase in exposure dose, confirming our earlier conclusion that the PAS acts as a negative tone photoresist with TBAH developer. The contrast (γ) and sensitivity (E_1) values of the PAS resist were calculated as ~0.08 and ~37.7 mJ/cm^2, respectively.

In perspective, the popular organic n-CAR, PMMA, is reported to pattern 20 nm features at an EUV exposure dose of 150−550 mJ/cm^2.[25] Similarly, organic n-CARs based on poly-4-hydroxy styrene derivatives were reported to print 50 nm line patterns with higher dose value under EUVL.[26] Therefore, we believe that the present resist system holds good potential for high-resolution EUV patterning applications.

In summary, we have shown the applications of a member of the polyarylenesulfonium polymer family, PAS, as a versatile n-CAR for NGL applications. The micro- and nanopatterning

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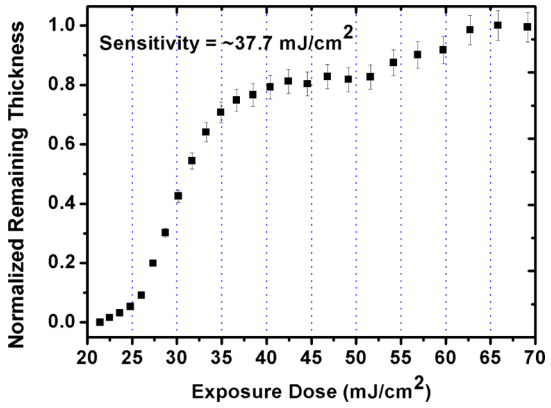

Figure 4. NRT vs EUV dose characteristics of the PAS resist.

properties of PAS were investigated by using i-line and EUV lithography tools, respectively, which revealed the excellent potentials of PAS to pattern 5 μm−20 nm line features with 1:3 line/spaces. The contrast (γ), center dose, and sensitivity (E_1) of PAS resist were 0.08, 17.6 mJ/cm^2, and ∼37.7 mJ/cm^2, respectively, which are comparable to or better than those reported for some of the organic n-CAR resists. Moreover, PAS could pattern highly dense and complex features such as nanodots, nanorings, and star-elbow features under EUVL conditions. The LERs of 30 nm line patterns at 1:4 line/space were calculated as 3.6 ± 0.3 nm. These initial experimental findings clearly reveal that the polyarylenesulfonium family of polymers has excellent potential to act as n-CARS for high-resolution (∼20 nm) lithography applications under EUVL conditions.[27]

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.6b10384.

Experimental data for PAS, optical and AFM images of PAS films, film thickness measurement data, and proposed mechanism for PAS resist action (PDF)

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Notes

The authors declare no competing financial interest.

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