

New High Resolution Resists for EUV Lithography

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Primary CNF Tools Used: ASML PAS 5500/300C DUV Wafer Stepper, JEOL 6300 E-Beam Lithography, P10

Abstract:

Extreme ultraviolet lithography (EUV) lithography is a very important technology for achieving the patterning goals of advanced lithography nodes with sub-15 nm feature sizes. Conventional chemically amplified photoresists (CARs) used in photolithography typically employ ionic photoacid generators (PAGs) which form superacids after exposure to light. In contrast, next generation double amplification resists (DARs) based on poly(4-bromophthalaldehyde) (PPA), employ non-ionic PAGs. In this report, the performance of developed trimellitic imide (TMI) non-ionic PAGs were evaluated using polymers prepared for CAR and DAR resist systems and their patterning performance was investigated using DUV (KrF) exposure and characterized by AFM and SEM microscopy. Comparative results indicate that the DARs displayed higher contrast and faster photospeed compared to the CARs. These findings highlight the potential of TMI PAGs for next generation PPA based DAR systems.

Summary of Research:

The continuous development by the semiconductor industry towards next generation nodes have raised the requirements of photoresist materials that can achieve resolution below the 20 nm scale with high photospeed below 20 mJ cm⁻².¹ Conventional chemically amplified resists (CARs) mostly utilize ionic PAGs which have high sensitivity and acid generation efficiency.²⁻³ However, self-immolative double amplification resists (DARs) have emerged as an attractive resist system due to their unique acid catalyzed amplification mechanism. Like CAR systems, DARs contain acid sensitive organic polymer poly(4-bromophthalaldehyde) (PPA) and PAG which generate protons after light exposure.

The generated proton catalyzes depolymerization of PPA into low molecular weight 4-bromophthalaldehyde monomer, which is readily soluble in organic solvents as shown in Figure 1.⁴⁻⁵

This rapid unzipping depolymerization mechanism of polymer to monomer requires catalytic amounts of acid, resulting in high sensitivity of DARs compared to CAR systems.⁶ Apart from these advantages, the higher sensitivity of DARs requires optimization of acid strength of PAGs to achieve balanced lithographic performance. In this case, non-ionic PAGs provide promising pathways for optimization, as their acid generation efficiency and acidity can be tailored by modifying molecular

structure. In this study, a series of TMI-based non-ionic PAGs were designed and synthesized. Further, these TMI PAGs were incorporated into CAR and DAR systems, and their lithographic performance such as sensitivity and patterning capability was systematically studied.

Result and discussion:

To evaluate the lithographic performance of CAR and DAR systems, polymer matrices and TMI PAGs with different substituents (as shown in Figure 2(a) and (b)) were formulated separately as CAR (1-5) and DAR (1-5). DAR formulation was prepared using cyclohexanone as a solvent whereas CARs employed a 50:50 PGME/PGMEA mixture. The resist thin film was prepared by spin-coating onto 4-inch silicon wafers to achieve a final film thickness of 50-70 nm. The coated films were soft baked on a hot plate at 70°C for 60 s (DARs) or 110°C for 60 s (CAR-5), followed by exposure using a 248 nm ASML stepper. After exposure, the wafers baked at 90°C (DARs) or 115°C (CAR-5) for 60 s. Further development was carried out using the isopropanol (DARs) or 2.38 wt% aqueous tetramethylammonium

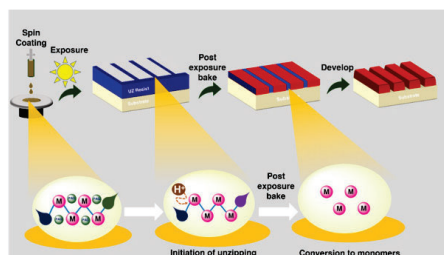


Figure 1: Lithographic process and depolymerization mechanism of PPA resist.

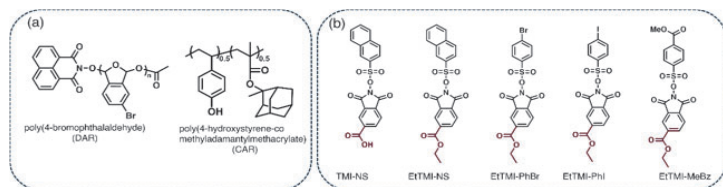


Figure 2: (a) Polymer matrices, (b) TMI PAGs used in this study.

hydroxide (TMAH) solution (CAR) and resulting film thicknesses were measured using ellipsometer.

The KrF contrast curves of the CAR formulations (Figure 3a) showed poor contrast for CAR-1 and CAR-2 whereas for CAR-3 to CAR-5 still required relatively higher dose-to-clear values. The poor contrast and reduced sensitivity are likely due to limited miscibility and weaker acid strength of TMI PAGs in CAR system. In contrast DAR formulations (Figure 3b) showed significantly higher sensitivity and faster photospeeds, particularly DAR-4 and 5.

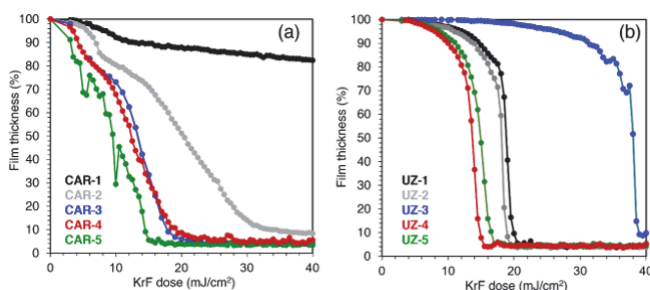


Figure 3: DUV contrast curves of (a) CAR (1-5), (b) DAR (1-5) formulations. Adopted from Ref.⁶.

As shown in Figure 4, the DAR systems exhibited different responses at an exposure dose of 25 mJ cm⁻², clearly demonstrating that the photospeed and acid strength of TMI PAGs can be tuned by modifying their substituents. DAR-3, which contained the least sensitive PAG, exhibited poor pattern formation under the same conditions. Even though TMI PAGs generally displayed low contrast with CARs, CAR-5 formulation successfully produced lithographic patterns, highlighting the versatility of TMI PAGs even in non-compatible systems. These obtained results are consistent with theoretical predictions of acid strength associated with different TMI substituent groups. By systematically changing the TMI substituents, we have successfully tuned photospeed of DARs, demonstrating clear structure-property relationship between PAG design and lithographic performance.

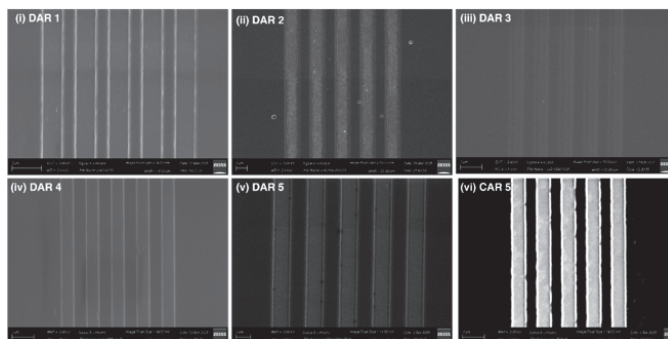


Figure 4: SEM images of (i-v) DAR (1-5) resist; (vi) CAR-5 resist using DUV lithography at exposure dose 25 mJ cm⁻². Adopted from Ref.⁶

Conclusions and Future Steps:

As a part of this work, we have developed series of TMI PAGs and investigated their sensitivity and patterning performance with both CAR and DAR systems. Based on theoretical and experimental results, iodine (EtTMI-PhI) and electron withdrawing (EtTMI-MeBz) based TMI PAGs are promising candidates in DAR resist system. Current efforts are directed toward PAG chain end initiators and PAG functionalized monomers to develop a single component PPA resist platform for next generation EUV lithography.

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