Scissionable Polymer Photoresist for Extreme Ultraviolet Lithography

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Primary CNF Tools Used: ASML 300C DUV stepper, ABM contact aligner, JEOL-9500 e-beam lithography, P10 profilometer

Abstract:

Researchers across the globe are intensively working on photoresists that can show high resolution down below 10 nm in a single-step process. Extreme ultraviolet (EUV) and electron-beam (e-beam) lithography are the most prominent candidates to create such small structures in resists. The difficulty in achieving such small feature size arises due to the RLS tradeoff, where the resists must simultaneously satisfy the resolution, line width roughness and sensitivity requirements. Also, another major concern with EUVL is the problem of stochastics due to lesser number of photons. Through our work, we believe that chemically amplified photoresists based on scissionable polymers are potential candidates to overcome these challenges. Our work focuses on polyaldehydes based low ceiling temperature (T_c) polymers that unzip upon exposure to DUV (deep ultraviolet)/EUV light sources due to main chain cleavage of the polymer backbones. So far, we have synthesized polyphthalaldehyde (PPA) based photoresists and studied their performances with the incorporation of various photoacid generators (PAGs) and base quencher.

Materials

Summary of Research:

One of the limitations with EUV light source is that there are much less photons available for the photochemical reactions of the photoresists. Either low or uneven light radiation energy across the exposed region can cause random defects during the lithography processes. Thus, it is desirable to pursue multimechanism photoresists that involves intrinsically depolymerizable polymers and the concept of chemical amplification. This approach shares some feature of the scissionable photoresist using main chain cleavage, but in contrast makes effective use of limited light exposure through the chain depolymerization of the resist polymer. The chain scissionable polymers usually have low ceiling temperatures (T_c) and contain weak chemical bonds, which can be cleaved by external triggers and thus starting the depolymerization process [1]. Due to their interesting properties, they have been widely utilized as sacrificial components in many areas, such as resist imaging, fabrication of porous materials, and transient electronics.

In our study, we focus on the synthesis of one kind of chain scissionable polymers, polyphthalaldehydes, via metal-free anionic polymerization of aldehyde monomers that are promoted by superbases bases with alcohol initiators [2]. Not only can this method produce linear PPA with tunable molecular weights and low dispersity, but also provides the possibility to introduce extra functional groups at the chain ends. Later, the PAGs can be introduced into the side chains using highly efficient post-polymerization reactions [3].

Materials and Methods; Synthesis:

Photoresist solution containing 5 wt.% PPA in cyclohexanone blended with common ionic and nonionic PAG's, for example, triphenylsulfonium triflate was prepared in varying ratios of 2-10 wt.% to PPA. Further base quenchers were introduced to these PPA-PAG blends [4]. The solution was then spin coated onto a silicon wafer at 3000 rpm for 1 min and post apply baked at 90°C for 1 min to remove excess solvent.

Results and Discussions:

The PAG blended polymer solution was exposed to 254 nm mid-UV radiation through a mask containing

patterns using ABM contact aligner. The pattern on the exposed resist was then directly observed through Nikon Microscope Cameras in CNF without the use of any developer or post-exposure processing techniques at different times after exposure. As shown in Figure 1, the image pattern continued to develop gradually over time. This is mainly because of the vaporization of monomers due to the main chain depolymerization under mid-UV radiations. Further the resist solution containing PAG, Base quencher blend was exposed to mid-UV radiations. As seen in Figure 2, good quality pattern was observed compared to the PAG only blended polymer patterns and the self-development of pattern was found to be more controlled.

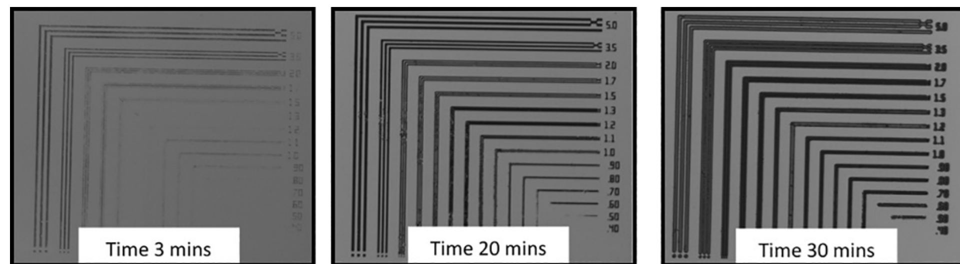

Figure 1: Optical microscope images of PAG blended PPA resist observed at different times after exposure to 1 mJ/cm² mid-UV radiation using ABM contact aligner.

Similar performance of these photoresists was also observed when exposed to 248 nm DUV radiation using ASML 300C DUV stepper. Well-defined 1:1-line spaced positive tone patterns were observed for an exposure dosage in the range of 1-4 mJ/cm² without any use of post-exposure. Further, these resists were evaluated under e-beam lithography using CNF JEOL 9500 Lithography tool. While large amounts of residues can be easily found at exposed areas, good 1:1 line patterns with feature sizes from 1000-400 nm were obtained for exposure dosage in the range of 75-100 µC/cm² by atomic force microscopy (AFM), as shown in Figure 3.

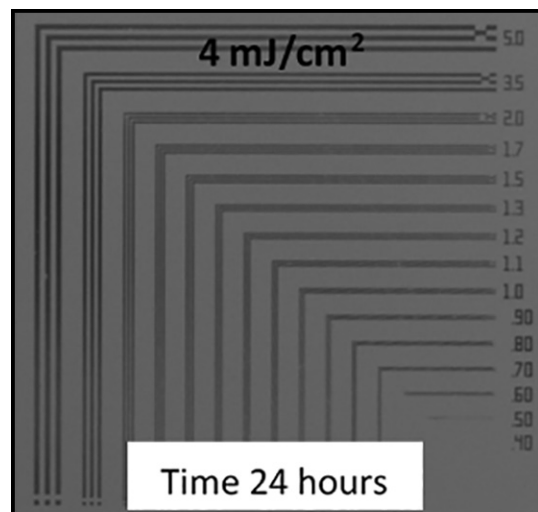

Figure 2: Optical microscope image of PAG, base quencher blended PPA resist observed at 24 hours after exposure to mid-UV radiation showing enhanced image quality.

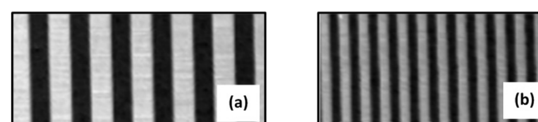

Figure 3: 1:1-line space patterns with feature size: (a) 600 nm (b) 400 nm observed under AFM after exposure to 75 µC/cm² e-beam radiation.

Summary:

In summary, photocleavable polymer photoresists show promising results when introduced to mid-UV, DUV and e-beam lithography. By introducing an optimized percentage of PAG and base quencher into resist solution, high contrast patterns under extremely low exposure dosages can be achieved. With these preliminary findings, PAG functionalized derivatives of PPA will be introduced to lithography, and the performances will be evaluated for achieving improved resolution and LER.

References:

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