**Development of Molecular Glass Photoresists for Next Generation Lithography**

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**Abstract**

In order to meet the growing demand of the electronics industry for smaller, higher resolution features, much attention has focused on next generation lithographic technique, such as extreme ultra violet (EUV) or e-beam lithography. Complementary to this field of research is the design of novel photoresist materials to produce sub-50 nm feature sizes. Chemically amplified molecular glass (MG) photoresists are among the most promising alternatives to traditional polymeric materials. A number of compounds which possess a rigid aromatic backbone were synthesized in our lab and evaluated for electron beam and EUV lithography. Herein, we describe the synthesis and lithographic evaluation of partially tert-butoxycarbonyl (t-Boc)-protected bulky phenol ‘CR1-60’. The resist CR1-60 is characterized by high glass transition temperature ($T_g \approx 130^\circ{}C$) and good film-forming properties.

**Summary of Research**

As the semiconductor industry moves to ever smaller feature sizes, extreme ultra violet (EUV) lithography is emerging as one of the most promising next-generation lithographic techniques for the production of sub-50 nm size features [1]. Photoresists designed for this wavelength must be more sensitive, in order to compensate for the typically low power of EUV light sources, and capable of producing high resolution features. In addition, they must fulfill low values of line edge roughness (LER). A recent advance in the design of photoresists has been the introduction of molecular glass (MG) resists [2]. Unlike conventional polymeric photoresists, MG resists are materials made up of small, discrete molecules rendered amorphous by functionalizing rigid core structures with bulky side groups [3].

In this report, we describe our work to develop a chemically amplified MG resist based on a bulky phenolic molecular structure (Figure 1). The structurally bulky phenol, CR-1, was prepared by conventional wet-chemistry processes and further protected with tert-butoxycarbonyl (t-Boc) group to produce a chemically amplified resist, CR1-60 [4]. Lithographic evaluation of CR1-60 was performed employing the tools at the Cornell NanoScale Science and Technology Facility (CNF) and Lawrence Berkeley National Laboratory (LBNL). The resist, CR1-60, was dissolved in propylene glycol mono-methyl ether acetate (PGMEA) containing triphenylsulfonium nonaflate as a photoacid generator (PAG). The resulting resist formulation was spin-coated onto a hexamethyldisilazane (HMDS)-primed wafer. No crystallization of the coated film was observed even after storage for several months, indicating the stability of the resist’s amorphous nature.

Positive-tone imaging properties were then tested under both deep UV (CNF) and EUV (LBNL) exposure conditions. These data are shown in Figure 2. CR1-60 resist...
is highly sensitive to UV light at 248 nm. A clearing dose of 0.32 mJ/cm² (E₀) was found experimentally. A post-applied bake (PAB) at 130°C was strongly required to ensure good quality of the resist film. SEM images demonstrated that sub-50 nm resolution could be achieved under EUV exposure conditions. A post exposure bake (PEB) at 80°C combined with the use of 0.26 N TMAH solution was a suitable condition to produce high quality patterns.

In conclusion, t-Boc protected MG resist, CR1-60, was synthesized and examined as a positive-tone resist for the next generation lithography. The bulky phenolic material has been found to be amorphous with a high enough glass-transition temperature (Tg) and a good alternative to conventional polymeric photoresists thanks to its uniformity in size and structure. Sub-50 nm features were produced successfully after patterning with EUV lithography.

References


