One-Component Molecular Glass Photoresists for EUV Lithography

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Primary CNF Tools Used: Zeiss Supra SEM, ASML 300C DUV stepper, ABM contact aligner

Abstract:

Extreme ultraviolet (EUV) lithography has entered into high volume manufacturing (HVM) phase in 2019. However, meeting the increased requirements for the photoresists still remains a challenge. As the feature size decreases, it is becoming more difficult to meet the requirements using conventional organic polymer-based chemically amplified resists (CAR). In this context, development of new photoresist material platforms with high resolution maintaining high sensitivity and low roughness is highly demanded. Our group has previously shown that molecular glass photoresist system has the excellent potential as a high-resolution photoresist platform. We are currently attempting to improve the performance of molecular glass photoresist by introducing photoacid generator (PAG) moieties into the resist molecules, making it completely one-component system. In this report, our preliminary results of deep ultraviolet (DUV) patterning with newly developed one-component molecular glass photoresists are described.

MATERIALS

Summary of Research:

Introduction. EUV lithography has already been in HVM phase. Throughout the next decade, a resolution of sub-10 nm half pitch (HP) will be the industry-wide target. In the era of sub-10 nm HP, which is comparable with polymeric materials, it is obvious that conventional CAR system reaches the technical limitation.

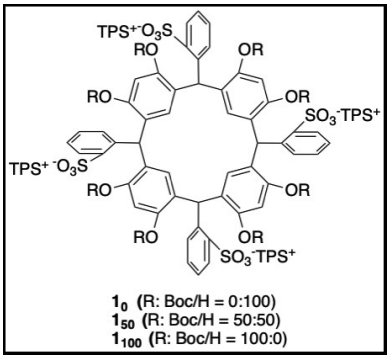

Figure 1: Chemical structures of the molecular glass photoresists used in the study.

Our group has previously reported utilization of amorphous small organic molecules, known as molecular glasses, as new photoresist platform [1,2]. Smaller, well-defined size of molecular glass resists compared to CAR was shown to be advantageous for achieving high resolution and low roughness patterning. However, perfect uniformity in component has yet to be achieved, as the previous systems required PAG as additive. In this work, we are attempting to develop completely one-component molecular glass photoresists, assuming that perfect uniformity in component as well as in size will give more homogeneous films, and therefore high resolution and low roughness patterning.

Material Design and Synthesis. Photoresist material has to meet several requirements including solubility, film forming ability and etch resistance. Especially for molecular glasses, which has low molecular weight and therefore higher tendencies to crystalize than polymers, additional care for crystallization should be paid because it will cause pattern deformation in lithography. To prevent crystallization, it is important to keep glass-transition temperature (T_g) much higher than temperature in post- and pre-exposure baking steps.

We have previously demonstrated that resorcin[4]arene-based molecular glass photoresists show high T_g due to its rigid and phenolic structures [2]. Herein we designed and synthesized novel one-component molecular resists by introducing PAG moieties on the rim of resorcin[4] arene core in varying substitution degree (Figure 1). The sulfonate groups were covalently bounded to the core in order to limit the diffusion of generated photoacid. The synthesis can be done only in three steps from reasonable commercially available reagents and basic laboratory techniques. This would allow feasible industrial scale production at low cost.

The synthesized photoresists could be dissolved in gamma-butyl lactone (GBL), a common spin-coating solvent regardless of their degree of substitution.

The solutions in GBL remained clear and did not give any precipitation even after one months at room temperature.

Photolithographic Performance Evaluation. Thin films could be fabricated by spin-coating 5 wt% GBL solutions onto unprimed 4-inch silicon wafers. The formed films did not show any obvious cracks. DUV exposure was performed using ABM contact aligner equipped with 248 nm filter and the exposed films were developed using isopropanol (IPA). Obtained pattered films were observed with optical microscope (Figure 2). Although much more improvement needs to be made, the microscopic images showed vague positive-tone patterns obtained without any PAG as additive. These preliminary results encourage us to explore one-component molecular glass system more.

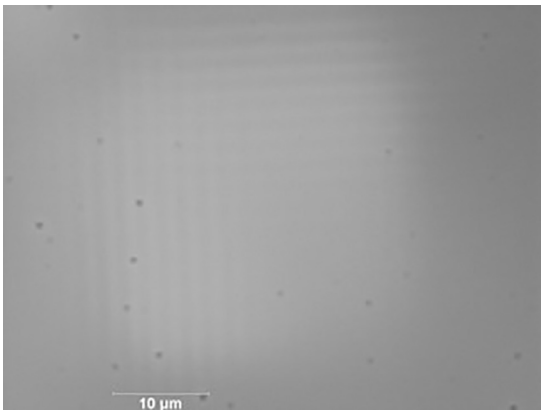

Figure 2: Optical microscope images of patterned film with 150. Prebake: 150°C/60s; Exposure: 20 mJ/cm^2; Development: isopropanol 120s.

Conclusions and Future Steps:

Novel resorcin[4]arene-based one-component photoresist materials have been successfully synthesized. They showed good film formation and positive-tone patterning ability with DUV exposure. Further improvements to obtain high contrast pattern from both material and process sides is underway.

References:

[1] J. Dai, S. W. Chang, A. Hamad, D. Yang, N. Felix, C. K. Ober Chem. Mater. 2006, 18, 3404-3411.

[2] S. W. Chang, R. Ayothi, D. Bratton, D. Yang, N. Felix, H. B. Cao, H. Deng, C. K. Ober J. Mater. Chem. 2006, 16, 1470-1474.