A novel molecular resist molecule was prepared by incorporation of 1,8-diazabicycloundec-7-ene into a tert-butylloxycarbonyl protected phenol malonate group. The resist shows high-resolution capability in both extreme ultraviolet (EUV) and electron beam lithography.

Keyword: molecular photoresist, extreme ultraviolet, electron beam, lithography

1. Introduction

Over the years molecular resists have received considerable interest as they have been proposed as a possible route to reducing the line edge roughness (LER) in photoresists as the line widths have reduced. The potential benefit of a small base unit with monodisperse size distribution in terms of dissolution uniformity and hence lower LER has been explored in several different molecule designs. Chemically amplified resists (CARs) using molecules such as calixarenes [1], noria [2], epoxide [3], xanthendiol [4] or fullerenes [5] have been developed to investigate this material class. In addition to these organic molecular resists, recently a non-chemically amplified material consisting of organometallic molecules has been presented [6]. While all of these materials have shown good lithographic properties, they have not been able to outperform polymeric CARs so far and for the promise of molecular resists to be fulfilled more work is required.

Our group started working in this field with the development of a fullerene based non-amplified negative tone molecular resist for electron beam lithography [7], which was capable of very high resolution but lacking the sensitivity of a CAR. The fullerenes were later functionalized to allow chemically amplification in both positive and negative tone [8, 9]. The resist design was then adapted towards EUV lithography [10]. With some modifications the system was able to resolve down to 16 nm half pitch patterns at a dose of 15-20 mJ/cm$^2$ with an LER of 5-6 nm [11]. During the course of optimizing the molecule structure and synthesis process of the fullerene system a new molecule herein referred to as “xMT” was synthesized. The xMT does not require the use of fullerenes for the synthesis reducing the cost of the material while exhibiting similar lithographic properties. It has been extensively studied for performance in e-beam and EUV lithography and the results of this investigation are presented here.
2. Experimental

2.1. Materials

The xMT molecule was produced by reacting 1,8-diazabicyclocoundene-7-ene with tBOC-protected phenol on a malonate chain. As it was not possible to fully confirm the final structure, Figure 1 shows the three possible configurations of xMT with the first structure shown being the most likely.

2.2. Sample Preparation

All samples were spun on silicon chips coated with a proprietary carbon underlayer. Prior to coating of the underlayer, the substrates were cleaned by a three-step process in (1) 10 min in isopropyl alcohol (IPA) in an ultrasonic bath, (2) 10 min in 1:1 solution of H$_2$SO$_4$:H$_2$O$_2$ and (3) 2 min in 0.1-1% hydrofluoric acid.

The fully formulated xMT resist consists of the xMT molecule, tris(4-hydroxyphenyl) methane triglycidyl ether crosslinker, triphenyl sulfonium hexafluoro antimonate photoacid generator and triphenyl sulfonium tosylate as a nucleophilic quencher. The individual components were dissolved in ethyl lactate and combined in a weight ratio of 0.2:2:1:0.16. Spin speed and solution concentration were adjusted to give a film thickness of 20-25 nm. After spin coating the samples received a post application bake (PAB) of 60°C for 3 min and after exposure the samples received a post exposure bake (PEB) of 90°C for 1 min. They were subsequently developed in n-butyl acetate for 60 sec and rinsed in IPA.

2.3. Lithography

The materials were exposed by electron beam at different acceleration voltages. 30 kV exposures were performed on a FEI XL 30 SFEG scanning electron microscope with ELPHY Plus pattern generator (RAITH GmbH). 100 kV exposures were done on a JEOL JBX-6300FS e-beam writer. EUV exposures were performed on the XIL-II interference lithography tool at the Paul Scherrer Institute, Switzerland. The XIL tool does not allow measurement of the dose at the wafer level and hence has to be calibrated against a reference resist with known dose to size [12]. For features smaller than the resolution limit of the calibration resist, dose was estimated from larger pitch sizes. Exposed samples were analyzed with a scanning electron microscope in top-down view. Where possible the images were analyzed with the software package SUMMIT [13] to extract the critical dimension and LER values.

3. Results and Discussion

The xMT material shows very high-resolution capability in electron beam exposure. For 30 kV acceleration voltage dense features with a pitch size as small as 26 nm were successfully patterned (Figure 2).

The material also has a low line width roughness (LWR), e.g. at 32 nm pitch a LWR value of 2.4 nm was measured at a line dose of 354 pC/cm. It is possible to increase the sensitivity of the material by substituting the crosslinker for a small novolac epoxy, which decreases the dose-to-size to about 214 pC/cm but at the expense of LWR and resolution. Examples are shown in Figure 3.

![Figure 2 Highest resolution of a 30 kV exposure of xMT](image)

![Figure 3 30 kV exposure of xMT with (left) novolac epoxy and (right) molecular epoxy](image)
In the case of 100 kV acceleration voltage nested square dense features could also be patterned down to 26 nm pitch size, although there is some pattern collapse evident at those sizes. At the 30 nm pitch a line dose of 1195 pC/cm was required to write the features. As expected the dose requirement is higher then for 30 kV as the backscattered background dose is decreased. Examples with both crosslinker types are shown in Figure 4.

The same high-resolution performance found in ebeam lithography was also seen in EUV. The examples in Figure 5 show well-resolved patterns at 32 nm pitch (30 mJ/cm², LER 2.15 nm) and 28 nm pitch (35 mJ/cm², LER 3.2 nm). Patterning at 22 nm pitch was also observed at about 50 mJ/cm². While not fully rendered, it is clearly more than modulation and formed lines are seen. We are in the process of optimization to improve the results at this pitch size.

Our working hypothesis for the patterning mechanism of xMT is that it efficiently controls the crosslinking of the epoxy preventing the crosslink network from extending outside the illuminated areas and hence suppressing bridging and creating smoother lines than a control resist without the xMT.

4. Conclusion

The molecular resist discussed in this paper exhibits high-resolution patterning. While molecular resists have generally struggled to really demonstrate advantages over more conventional polymeric resists, the xMT shows lithographic properties close to ITRS targets for high volume manufacturing, indicating that molecular resists can be a viable alternative to more conventional CARs. As patterning at 22 nm pitch was seen and further optimization work is ongoing, the ultimate resolution of this material is yet undetermined and could possibly extend into the single nanometer regime.

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