Photobleaching Nonchemically Amplified Photoresists

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Introduction

Chemically amplified resists (CARs) utilizing acid-catalyzed reactions have been widely used for the production of integrated circuits. Despite of their high photosensitivity, the chemically amplified resists suffer from serious problems such as the appearance of an anomalous insoluble skin layer and line-width shift caused by the air-borne contamination and the acid diffusion in the resist films when the post-exposure bake is delayed. These post-exposure delay (PED) problems make it difficult to fabricate fine patterns [1]. Nonchemically amplified resists have a greater potential to suppress these PED problems as they are not susceptible to air-borne contamination and acid diffusion.

We have designed and synthesized nonchemically amplified polymeric and molecular resists and evaluated their lithographic performance for deep UV lithography. As the feature size of the patterns keeps on shrinking to the molecular dimensions, molecular resists, that utilize smaller building blocks compared to the polymeric resists, are gaining more attention due to their high resolution capability and less line edge roughness [2].

Results and discussion

Synthesis of polymeric and molecular resists. Figure 1 shows the synthetic schemes of the polymeric and molecular resists. The monomer 2-(2-diazo-3-oxo-butyryloxy)-ethyl methacrylate (DOBEMA) was synthesized from 2-(methacryloyloxy)ethyl acetoacetate, which was further copolymerized with γ-butyrolacton-2-yl methacrylate (GBLMA) by free radical polymerization [3]. For the molecular resist, polyhedral oligomeric silsesquioxane (POSS) was chosen as silicon-containing component because POSS molecules are thermally and physically more robust than silicones and are easy to functionalize [4]. To synthesize the molecular resist, 3-diazo-3-ethoxycarbonyl-2-oxo-propyl ester (CDEOPE) was treated with octa(chlorodimethylsilylethyl)-POSS to obtain CDEOPE-POSS.

Photobleaching studies. The photobleaching degree of the polymeric and molecular resist materials was calculated by measuring the absorbance coefficient values of the resist materials before and after UV light irradiation. Upon irradiation, the absorbances of the polymeric resists of DOBEMA were decreased by 72.9-93.6% at 248 nm and 61.6-81.9% at 193 nm, whereas the absorbances of the molecular resist (CDEOPE-POSS) were decreased by 81.4% at 248 nm and 13.2% at 193 nm. All the resist materials reported in this study contain diazoketo groups that upon irradiation of deep UV light undergo Wolff rearrangement to generate the carboxylic groups and thereby offering the solubility change. The mechanism of the solubility change was confirmed by Infrared spectroscopy and ^{13}C NMR studies. The elimination of the diazo functional group upon UV light irradiation is the cause of photobleaching in these resist materials.

Lithographic evaluation. A resist solution of the polymer was prepared by dissolving 0.2 g of poly(DOBEMA-co-GBLMA) in 1.4 g of cyclohexanone and coated onto a hexamethyldisilazane-treated silicon wafer by spin-coating. The resist solution of the molecular resist was prepared by dissolving 0.2 g of CDEOPE-POSS in 1.6 g of propylene glycol methyl ether and coated onto a hexamethyldisilazane-treated silicon wafer by spin-coating. Exposure was carried out with a mercury-xenon lamp in a contact printing mode. The exposed wafer was developed by rinsing in a 2.38 wt.% tetramethylammonium hydroxide aqueous solution. Figure 2 shows the scanning electron micrograph images of the 0.7 μm line and space patterns obtained with poly(DOBEMA-co-GBLMA) and CDEOPE-POSS. The molecular resist, CDEOPE-POSS, possesses a very high oxygen reactive ion etching (O_2-RIE) resistance, which is an essential criterion for a resist material to be used as a bilayer resist. Bilayer resists have several advantages. Because the top imaging layer is very thin, the resist materials of relatively high absorbance can also be used. The anti-reflective bottom planarizing layer diminishes the defects like standing wave effect, which causes irregular line edge profile. Furthermore, bilayer resists need only a small depth of focus and high aspect ratio patterns can be obtained. Figure 3 shows the scanning electron micrograph image of 0.7 μm line and space pattern obtained with CDEOPE-POSS as a bilayer resist, after O_2-RIE. Novolac was used as the planirizing layer.

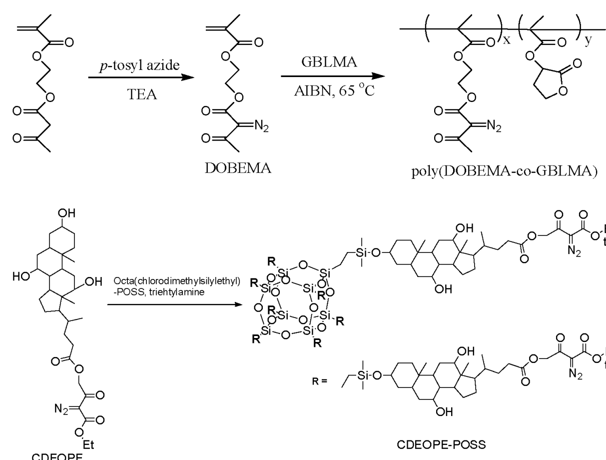

Figure 1. Synthetic schemes of poly(DOBEMA-co-GBLMA) and CDEOPE-POSS.

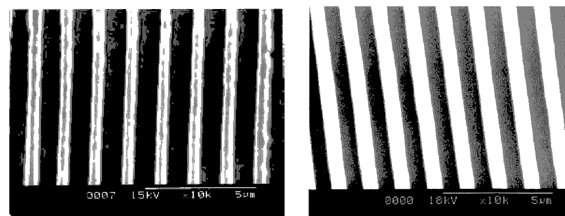

Figure 2. Scanning electron micrograph images of 0.7 μm L/S patterns formed with poly(DOBEMA-co-GBLMA) and CDEOPE-POSS, respectively.

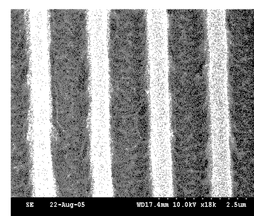

Figure 3. Scanning electron micrograph image of 0.7 μm L/S positive tone image, formed with CDEOPE-POSS and novolac as a bilayer resist after O_2 plasma etching.

Conclusions

We designed and synthesized new type of nonchemically amplified polymeric and molecular resists and studied their lithographic performance. These resist materials showed high photobleaching effect at 248 nm and moderate to good photobleaching effect at 193 nm. The lithographic studies of these materials showed their potential to be used as single and bilayer resists.

References

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