The Impact of Fluoropolymers on Line Edge Roughness in 193 nm Imaging

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We report here a family of tetrafluoroethylene (TFE) based photoresist polymers that image at 193 nm with low line edge roughness relative to other candidate polymers, while also demonstrating good resolution, high contrast, high transparency at the imaging wavelength and widely tuneable dissolution rates. These polymers are typically composed of (TFE), cyclo-olefins such as norbornene with one or two pendant hexafluoroisopropanol groups per monomer and various acrylates. A solubility switch is incorporated into either the cyclo-olefin or the acrylate monomers. These polymers have the flexibility to easily incorporate a wide range of monomers to enhance properties such as solubility and adhesion. Imaging using Lucent's 0.6 NA SVGL stepper with an altPSM is shown. Contrast, optical absorption and dissolution data are also discussed. We have demonstrated a process for manufacture of these polymers that is scaleable to commercial volumes and which results in exceptional compositional uniformity and acceptably low levels of impurities.

Keywords: TFE, photoresist, line edge roughness, dissolution rate

1. Introduction

A wide variety of polymer platforms such as (meth)acrylate copolymers, (meth)acrylate copolymers functionalized with pendant alicyclic groups, cycloolefin-maleic anhydride copolymers, etc. have been developed for use in photoresists for 193 nm imaging. While several of these photoresists have been used very successfully to allow the semiconductor industry to begin production of devices using 193 nm imaging, as more demanding nodes are encountered, some fundamental limitations of these resists, such as line edge roughness, become increasingly important.

Over the past few years, DuPont has developed a family of TFE based copolymer resins that have been shown to provide a balance of functional properties of importance in application in 157 nm resists. We have now extended this platform to polymers designed specifically for 193 nm resists.

fluoroalcohol (NbFOH) which provides aqueous solubility and etch resistance and one or more solubility switches. In addition to the switch, other groups (generally acrylates and/or methacrylates) may be added to improve adhesion, etch resistance and resolution. Some or all of the norbornene may also be protected to control $R_{\min}$ and $R_{\max}$. Details of the synthesis of these, similar polymers, and some of the fluorinated monomers have been previously published.[1]

Fig. 1 Polymer structure

2. Polymer Structure

A wide range of polymers having the general structure shown in Fig. 1 have been investigated. All of the polymers include TFE, which functions as a transparent linker of the other comonomers in the system, norbornene

Typically, photoresists are created from these polymers by formulating them with a triphenylsulfonium nonaflate photoacid generator and a tetrabutylammonium lactate base. Standard

formulation solvents are 2-heptanone, ethyl lactate and PGMEA.

3. Polymerization

As line edge roughness (LER) has become more important in the overall function of 193nm photoresists, many explanations for the fundamental source for the roughness have been proposed. It has been generally agreed that one contributor to LER may be non-random distribution of monomer units in the polymer (either within a single chain or from chain to chain). Such compositional non-uniformity can translate directly to variations in the concentration of switches in the polymer. A typical photopolymer will contain ~ 20% - 30% switch. Since relatively small changes in the degree of protection can result in vastly different dissolution rates, local variations might lead to LER. Consequently, it is critical that the monomers be selected and the polymerization be controlled so that polymer non-uniformity is minimized.

In the all-methacrylate platform, for example, comonomers can be selected to reduce the differences in relative polymerization reactivity as a means to impact compositional uniformity. For all of the TFE copolymers of interest, however, there are extremely very large differences in reactivities in the monomers. We have shown, however that by using a closed-loop polymerization process in which the liquid phase composition is continuously monitored and regulated, polymers having exceptionally high uniformity and randomness may be prepared. We have now demonstrated this process technology to be reproducible, scalable and clean by photoresist polymer standards.

4. Imaging

Imaging was done using Lucent's SVGL stepper. An AltPSM mask was used with optics configured to $NA = 0.60$ and $\Sigma = 0.3$. Samples were coated on AR19 ARC and developed using 0.26N Clariant 300MIF developer. Top-down SEM's were made using a KLA Tencor 8100 CD SEM. Cross-SEM's were made using a JEOL 6700F Field Emission SEM.

A wide variety of monomer combinations having the TFE / NBFOH / acrylate structure were examined. The imaging performance of these polymers are represented by the results of one such polymer, shown in Fig. 2.

Fig. 2 Top-down and cross-section SEM images of 100 nm 1:1 lines in a TFE / NBFOH / Acrylate resist

5. Line-Edge Roughness (LER)

Determining quantitative LER values that can be associated with a photopolymer is notoriously difficult. Measured values of LER can depend not only on inherent properties of the photoresist such as the photopolymer and formulation additives (PAG, base, surfactants, etc.) but also on image contrast, film thickness, SEM resolution, image analysis parameters and length of the analyzed line. Despite all of these potential contributors to variability, most LER values reported for non-TFE photopolymers fall in the range of 6- 8 nm, consistent with values we have obtained for the best non-TFE photopolymers we have examined. Using the same formulation additives, imaging conditions and analysis methods we find the LER of the TFE based photopolymer resists to be 4.5 - 6 nm. A comparison between two of the best resists from each class is shown in Fig. 3. We conclude that these TFE-based polymers provide a measurable improvement in LER relative to other polymer platforms for 193nm imaging.

Fig. 3 Comparison of 100 nm 1:1 lines in developed

6. Dissolution

Dissolution contrast, the maximum dissolution rate ($R_{\max}$) and the minimum dissolution rate ($R_{\min}$) must be controlled for optimal resist performance. Fig. 4 and Fig. 5 show dissolution data for TFE / NbFOH / Acrylate resists. Fig. 4 shows the clean onset of solubility with dose that is expected to minimize rounding of features and the complete clearing at slightly higher dose that is expected to minimize footing. The rate curve (Fig. 5) demonstrates high contrast ($\gamma = 10$) and high $R_{\max}$. The flexibility of the TFE-based polymer design allows control of both $R_{\min}$ and $R_{\max}$ to optimize resist performance.

Fig. 4 Thickness vs. dose for a TFE / NbFOH / Acrylate resist developed for 60 sec.

7. Conclusions

A polymer platform based on TFE and norbornene fluoroalcohol has been developed which provides significant advantages over other candidate polymers for use in 193nm photoresists. Significantly, this platform results in line edge

Fig. 5 Dissolution rate vs. dose for a TFE / NbFOH / Acrylate resist

roughness (LER) that is improved by as much as 50% over the best reported values obtained with other candidate polymers. Contributing to this LER advantage are the inherent nature of the fluorinated system, a process technology that results in higher compositional uniformity and the well-behaved dissolution of the system. The process of manufacture for these materials has been demonstrated to be extremely reproducible, scaleable and clean. The combination of product design flexibility, lithographic performance and manufacturability of this polymer platform should make it a leading candidate for commercialization at the leading nodes of 193 nm lithography.

Reference

1. A.E. Feiring et al., *Journal of Fluorine Chemistry*, **122** (2003) p11–16