Preparation and Lithographic Performance of Novel Copolymers Having Acid Labile Pendant Alicyclic Ether Moieties

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Abstract: A series of methacrylic copolymers derived from methacrylic acid (MAA), methyl methacrylate (MMA), n-butyl methacrylate (BM), and bornyl methacrylate (BMA) with various feed molar ratios was synthesized. In order to introduce acid labile alicyclic ether groups, the pendant carboxyl groups of copolymers were further functionalized with unsaturated alicyclic ethers of 2,3-dihydrofuran (DHF), 3,4-dihydro-2H-pyran (DHP), and 3,4-dihydro-2-methoxy-2H-pyran (DHMP). The existence of alicyclic bornyl groups was found to increase the thermal and plasma etching resistance of polymers but to decrease the sensitivity and contrast. Copolymers having pendant carboxyl groups can be crosslinked in the presence of photoacid after sufficient heat treatment. Acid catalyzed dehydration of pendant carboxylic acids may also cause the crosslinking of polymers. The thermogravimetric properties of copolymers, exposure characteristic curves and lithographic evaluation of the positive tone photoresist were all investigated. A line and space pattern resolution of 0.3 μm was also achieved.

Keywords: Photoacid generator, Chemical amplified reaction, Photoresist, Alicyclic ether, Acid labile Groups, Acid catalized dehydration.

Introduction

Chemical amplification photoresists using photoacid generators (PAG) have attracted increasing attention as catalysts for high sensitivity photoresist systems [1-3]. Deep-UV lithography is one of the most promising technologies for sub-quarter micron feature delineation [4-8]. Most of the resist materials available contain aromatic rings that provide good dry etching resistance. Resists of this kind, however, cannot be used for ArF lithography due to the great UV absorbance of the aromatic ring at the 193 nm. Since acrylic polymers have a sufficient transparency at 193 nm wavelength, the polymers could serve as a polymer matrix for deep-UV photoresists [9-13]. Poor dry-etching resistance is one of the disadvantages of the acrylic polymer resists.

Carboxyl groups are often protected by reaction with unsaturated cyclic ether, which yields esters that are stable toward base and many other reagents but easily hydrolyzed by acids [14-16]. In our previous paper [4], we reported a novel acid catalyzed dehydration crosslinking for negative tone photoresists comprising copolymers having pendant carboxyl groups. The physical properties of the relief polymeric patterns were improved effectively due to the dehydration crosslinking of the pendant carboxyl groups.

In this article, we discuss the synthesis of a series of methacrylic copolymers derived from methacrylic acid (MAA), methyl methacrylate (MMA), n-butyl methacrylate (BM), and bornyl methacrylate (BMA) with various feed molar ratios. The pendant carboxyl groups were further functionalized with unsaturated alicyclic ethers. The following were also investigated: the thermogravimetric properties of copolymers, exposure characteristic curves, lithographic evaluation of the positive tone photoresists, and the effects of alicyclic groups on the plasma
etching resistance of copolymers.

Experimental

1. Materials

Methacrylic acid (MAA), methyl methacrylate (MMA), n-butyl methacrylate (BM), bornyl methacrylate (BMA), 2,3-dihydrofuran (DHF), 3,4-dihydro-2H-pyran (DHP), and 3,4-dihydro-2-methoxy-2H-pyran (DHMP) were purchased from Acros and purified by general methods. Triarylsulphonium salt, used as the ionic photoacid generator (PAG), was purchased from Aldrich. The initiator azobisisobutyronitrite (AIBN) was purified by recrystallization in ethanol. The organic solvents used in this investigation were all distilled and dried with molecular sieves prior to use.

2. Measurements

The UV-visible spectra of films of the photore sist on quartz substrates were measured with a Jasco UV/Vis 7850 double-beam spectrometer. The photore sist was exposed with a Karl Suss MJB-3 aligner. The film thickness was measured with a Tencor Instrument alpha step-200 film thickness monitor. The dissolution rate was defined as the change in the photore sist film thickness per development time. The resist pattern profiles were evaluated using a Jeol JSM-35 and JAX-840 scanning electron microscope. Thermal properties and functional groups of polymers were evaluated and analyzed using a Du Pont 910 differential scanning calorimeter, Perkin-Elmer TGA-7 thermogravimetric analyzer, and Jasco FTIR spectrometer. Elemental analysis was carried out with a Heraeus CHN-O rapid elemental analyzer. A TOA pH meter was used to measure the pH values of developing aqueous solutions.

3. Preparation and functionalization of copolymers

Copolymers were obtained by the copolymerization of monomers in tetrahydrofuran (THF) in the presence of 1 wt% AIBN at 60 °C for 12 h. Copolymers were poured into a glass polymerization tube equipped with a sealing cap, which was degassed in a vacuum by using a freeze-thaw technique and then sealed off. After complete polymerization, copolymers were precipitated from a large amount of water/methanol (1/1 in volume) solution and then thoroughly washed with distilled water. In order to introduce the pendant alicyclic groups, copolymers dissolved in tetrahydrofuran (THF) with excess unsaturated cyclic ether were poured into a glass tube equipped with a sealing cap and then sealed off.

The mixture was heated at 70 °C for 24 h, precipitated by pouring the reaction mixture into a large amount of distilled water, and then washed with the distilled water.

4. Lithographic evaluation

A photo resist solution was prepared by dissolving copolymers (1.5 g) and triarylsulphonium hexafluoroantimonate (photoacid generator, 0.15 g) in 10 mL THF. The photosensitive solution was filtered through a 0.45 μm filter and then spin coated onto a silicon wafer plate at 1,000 r.p.m. for 10 s followed by 2,500 r.p.m. for 20 s. It was then prebaked at 90 °C for 2 min. The photo resist was exposed with a Karl Suss MJB-3 aligner. After exposure for 1 min, the resist was post-exposure baked (PEB) at 110 °C for 2 min and then developed through 20 s of immersion in 0.1 wt% sodium carbonate developer. A clear pattern was obtained when the exposed resist was rinsed thoroughly with distilled water. The relief polymeric materials were then exposed with UV light and then further heat treated at 150 °C for 60 min. At this stage, the dehydration of pendant carboxyl groups occurred, leading to the crosslinking of copolymers. Resolution of the photo resist was estimated by the SEM technique.

Results and Discussion

Scheme 1 shows the structure of the copolymers synthesized in this investigation. In polymers, MAA plays an important role in a resist's ability to be base-developable. BM was introduced to provide good adhesion on the silicon substrate and to improve the developing properties. BMA was utilized to improve the dry etching resistance.

The results of the polymerization of comonomers are summarized in Table I. All polymers shown in Table I can be dissolved in an alkaline aqueous solution. As can be seen, polymer 1 without the bornyl methacrylate (BMA) unit has a relatively higher thermal resistance. The feed monomer content of BMA in polymer 2, 4 and 3, 5 are 20 and 25 mol%, respectively. As shown in Scheme 1, the