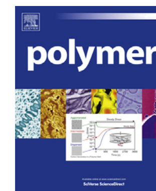
Polymer 55 (2014) 3599–3604

Contents lists available at ScienceDirect

Polymer

journal homepage: www.elsevier.com/locate/polymer



Triphenylsulfonium salt methacrylate bound polymer resist for electron beam lithography

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ARTICLE INFO

Article history:
Received 14 January 2014
Received in revised form
31 May 2014
Accepted 3 June 2014
Available online 12 June 2014

Keywords:
Photoacid generator
PAG bound polymer
Electron beam lithography

ABSTRACT

A new photoacid generator (PAG) bound polymer containing triphenylsulfonium salt methacrylate (TPSMA) was synthesized and characterized. The PAG bound polymer was employed to improve electron beam lithographic performance, including sensitivity and resolution. The PAG bound polymer resist exhibited a higher sensitivity (120 μC/cm^2) than the PAG blend polymer resist (300 μC/cm^2). Eliminating the post exposure baking process during development improved the resolution due to decreased acid diffusion. A high-resolution pattern fabricated by electron beam lithography had a line width of 15 nm and a high aspect ratio. The newly developed patterns functioned well as masks for transferring patterns on Si substrates by reactive ion etching.

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1. Introduction

Microelectronic industries continue to make rapid progress in the development of new technologies. In particular, there has been a great deal focus on developing lithographic techniques for reducing pattern size in the fabrication of high-density integrated circuits (IC) [1,2]. There are several leading nanofabrication lithographic techniques that are able to obtain high-resolution patterns with proper resist materials. Among the various lithographic techniques used to overcome the resolution limit of conventional lithography, electron beam lithography (EBL) is one of the most powerful candidates for obtaining microstructure pattern sizes smaller than 20 nm [3–6]. Mostly popular electron beam resist is poly(methyl methacrylate) (PMMA) [7] due to high resolution and easy processing characteristic. However, PMMA has a low contrast and poor dry etch resistance to get high throughput.

New lithographic materials are needed to meet the requirements of EBL applications. Specifically, the ideal resist should exhibit high sensitivity, high resolution, and good thermal stability during lithography processing as well as a low line edge roughness (LER). Chemically amplified resists (CARs) have emerged as a powerful candidate lithographic material because of their high sensitivity and high resolution. Practically, most CARs are blends of an acid reactive polymer such as an epoxy group based polymer and a photoacid generator (PAG) [8,9]. CARs are effectively amplified by the photo-induced acid generation within the exposed area of the resist film to increase or decrease the solubility in a specific developer solution [10].

However, blended CARs have a limited resolution and poor line edge roughness due to acid diffusion, non-uniform acid distribution, and acid migration during the post-exposure baking (PEB) process [11,12]. Indeed, controlling acid diffusion is critically important for distributing acid more uniformly throughout polymer resist. One of the methodologies used to overcome the problems associated with traditional CARs is to incorporate a PAG unit into the polymer side chain [13–15]. We already reported a novel chemically amplified positive photoresists, a terpolymer of methyl methacrylate (MMA)/*tert*-butyl 4-vinylphenyl carbonate (*t*BVPC)/triphenylsulfonium salt methacrylate (TPSMA) and a terpolymer of *tert*-butyl 4-vinylphenyl carbonate (*t*BVC)/*n*-[*p*-(*t*-butyloxycarbonyloxy) phenyl]maleimide (*t*BOCOPMI)/triphenylsulfonium salt methacrylate (TPSMA) [16]. Lithographic performance of a PAG bound polymer resist based on *tert*-butyl 4-vinylphenyl carbonate, *n*-[*p*-(*t*-butyloxycarbonyloxy) phenyl]maleimide terpolymers as a novel chemically amplified resist exhibited a positive working behavior and showed 0.18 μm line pattern at electron beam

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http://dx.doi.org/10.1016/j.polymer.2014.06.008
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lithography to indicate that the polymer bounded PAG resists have a potential to fabricate nanostructures.

In this paper, we present a new PAG bound polymer comprising glycidyl methacrylate (GMA), methyl methacrylate (MMA), and triphenylsulfonium salt methacrylate (TPSMA) for use in electron beam resist. We also compared the sensitivity and contrast characteristics of the PAG bound polymer resist with the PAG blend polymer resist. The PEB process conditions used to obtain patterns of high resolution and high aspect ratio in the lithographic process are also reported.

2. Experimental

2.1. Materials

Benzyl methacrylate (BMA), diphenyl sulfoxide (DPS), trifluoromethane sulfonic anhydride (TFMSA), glycidyl methacrylate (GMA), and propylene glycol monomethyl ether acetate (PGMEA) were purchased from Aldrich Chemical Co., Ltd. and used without any purification. Methyl methacrylate (MMA) was used after distillation to remove the inhibitor. 2,2′-Azobisisobutyronitrile (AIBN) was obtained from Wako Pure Chemical Industries Ltd. and recrystallized from methanol prior to use. Methylene chloride (MC) and tetrahydrofuran (THF) were supplied by Fisher Scientific Co., and before use were dried over sodium metal and distilled. Isopropyl alcohol (IPA), methanol and N,N′-dimethylformamide (DMF) were received from Fisher Scientific Co. and used without further purification. Four-inch commercial prime grade single crystal silicon wafers with a polished (p-type, 100) face were obtained from LG Siltron Co. Deionized water was purified to a resistance of 18.0 MΩ cm with a Milli-Q reagent grade water purification system (Millipore Co.).

2.2. Synthesis of triphenylsulfonium salt methacrylate (TPSMA) as a photoacid generator

A solution of 1.00 g (5.67 mmol) of benzyl methacrylate and 1.15 g (5.67 mmol) of diphenyl sulfoxide in 30 mL methylene chloride was slowly added to 1.15 mL of trifluoromethane sulfonic anhydride at −78 °C. The reaction mixture was then stirred for 30 min and the temperature was allowed to rise to room temperature. The solution was cooled again to 0 °C and 2.50 equivalents of MeOH in 2.0 mL of H_2O were slowly added. The methylene chloride layer was collected, evaporated, and then purified by silica gel column chromatography with a 20: 1 mixture of methylene chloride and methanol as an eluent to obtain 2.60 g of a yellow and sticky oil in 83% yield.

^{1}H NMR (400 MHz, $CDCl_3$): $\delta = 8.15$~7.80 (m, 14H, aromatic), 6.20 (s, 1H, C=C—H), 5.65 (s, 1H, C=C—H), 5.29 (s, 2H, O—CH_2), 1.97 (s, 3H, C—CH_3).

^{13}C NMR (100.6 MHz, $CDCl_3$): $\delta = 166.7$, 144.3, 136.2, 135.0, 131.9, 131.6, 130.4, 125.2, 124.5, 123.0, 119.8, 64.9, 17.8.

$C_{24}H_{21}S_2O_5F_3$ (510.54) Calc'd. C 56.46 H 4.15 S 12.56 F 11.16.

Found C 55.99 H 3.97 S 12.79 F 10.77.

2.3. Polymerization of poly((glycidyl methacrylate)-co-(methyl methacrylate)) (poly(GMA-co-MMA))

Poly(GMA-co-MMA) as a blend polymer with PAG was obtained by free radical polymerization in THF. Glycidyl methacrylate (3.35 g, 23.6 mmol), methyl methacrylate (9.43 g, 94.2 mmol), and 2,2′-azobisisobutyronitrile as a free radical initiator (3 mol% to the monomers) were dissolved in 350 mL of freshly distilled anhydrous tetrahydrofuran. Polymerization was performed at 66 °C for 24 h. The as-obtained polymer solution was precipitated in a large amount of hexane and dried under vacuum. Further purification was carried out by dissolving the product in THF followed by precipitation with hexane two times and drying under vacuum at 40 °C for 48 h. Yield 91.0%. The glass temperature and the decomposition temperature of poly(GMA-co-MMA) were 95.0 °C and 105.0 °C, respectively. The number-average molecular weight was 16,200 g/mol.

2.4. Polymerization of poly((glycidyl methacrylate)-co-(methyl methacrylate)-co-(triphenylsulfonium salt methacrylate)) (poly(GMA-co-MMA-co-TPSMA))

Poly(GMA-co-MMA-co-TPSMA) as a PAG bound polymer was synthesized according to conditions similar to those described for the synthesis of poly(GMA-co-MMA). Briefly, radical polymerization of glycidyl methacrylate (0.10 g, 0.70 mmol), methyl methacrylate (0.21 g, 2.11 mmol), and triphenylsulfonium salt methacrylate (0.36 g, 0.70 mmol) was carried out at 66 °C in 45 mL of dry THF for 24 h using 3 mol% of AIBN (0.11 mmol). The viscous polymer solution obtained was diluted with dichloromethane and sequentially filtered and precipitated using an excess amount of a 3:7 mixture of hexane and IPA. The precipitated solid was then filtered, washed with hexane and dried under vacuum. Further purification was achieved by repeating this process one to two times as needed. As-obtained poly(GMA-co-MMA-co-TPSMA) was dried under vacuum at 40 °C for 48 h. Yield 84.0%. The glass temperature and the decomposition temperature of poly(GMA-co-MMA) were 122.0 °C and 250.0 °C, respectively. The number-average molecular weight was 23,800 g/mol.

2.5. Characterization

^{1}H NMR spectra were recorded on a Varian UNITY INOVA (400 MHz) spectrometer in $CDCl_3$ using tetramethylsilane as an internal reference. Thermal analyses were performed using a TA Instruments DMA 2980 at a heating rate of 10 °C/min and a TA Instruments DSC 2910 at a heating rate of 5 °C/min under a nitrogen atmosphere. The molecular weights of the polymers were determined in hexafluoroisopropanol (HFIP) containing 0.01 N sodium trifluoroacetate with a Waters III instrument equipped with a refractive index detector. The thicknesses of resist films were measured with an ellipsometer (Rudolph Auto EL 2, USA). The heights of patterns were measured by atomic force microscope (XE-100 PSIA, Korea). The shapes of resist patterns were imaged by field emission scanning electron microscope (FE-SEM) (S-4700 Hitachi, Japan).

2.6. Preparation of resist films on silicon substrates

Resist solutions were prepared by first dissolving 4~10 wt% of polymer in DMF or PGMEA followed by filtration through 0.1 μm PTFE membrane filter (Whatman Co.). Resist films were prepared by spin coating the resist solutions onto silicon substrates at 3000 rpm for 40 s. Soft baking at 80 °C was performed 2 min to vaporize residual solvents and enhance the hardness of thin films. The thickness of spin-coated films was measured using an ellipsometer.

2.7. Evaluation of lithographic performance

The contrast and sensitivity of resists were evaluated using atomic image projection electron-beam lithography (AIPEL) [17]. Circular areas with a diameter of 30 μm were exposed to a range of electron doses between 50 and 2000 μC/cm^2 at an acceleration voltage of 100~200 keV. A post-exposure baking (PEB) process was

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