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Interface imaging process for high resolution and high aspect ratio patterning

Seung A. Woo [a], Ji Young Park [b], Su Min Kim [a], Jin-Baek Kim [a,*]

[a] Department of Chemistry, Korea Advanced Institute of Science and Technology (KAIST), 373-1, Guseong-Dong, Yuseong-Gu, Daejeon 305-701, Republic of Korea
[b] LG Chem, Ltd., 104-1, Moonji-Dong, Yuseong-Gu, Daejeon 305-380, Republic of Korea

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ABSTRACT

A novel interface imaging process is proposed for high resolution and high aspect ratio patterning. The photoresist system is composed of a top acid-labile silicon-containing polymer, an intermediate layer containing a photoacid generator, and a cross-linked bottom layer. Upon patternwise exposure to UV light, acid is produced in exposed areas of the intermediate layer. The acid diffuses into the top layer during the post-exposure bake and induces cross-linking of the silicon-containing polymer. After development of the top layer, the pattern is transferred into the bottom layer through an oxygen reactive ion etching. High resolution and high aspect ratio patterns were obtained by controlling the penetration depth of acid and the anisotropic reactive ion etching process.

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1. Introduction

Fabrication of smaller devices has become a current challenge in microelectronic, optoelectronic, and microelectromechanical systems. Patterning techniques, such as e-beam lithography, scanning probe lithography, and nanoimprint lithography, have permitted the fabrication of sizes down to less than 50 nm, overcoming resolution limits. Photolithography techniques have been widely used because they are fast, simple, and low-cost [1–6]. Due to these advantages, new techniques have been developed based on photolithography, such as molecular resist lithography, photolithography using selective chemisorption, and the eco-friendly resist system [7–9].

The chemically amplified resist (CAR) system using acid-catalyzed reactions has been widely used in semiconductor industries due to its high photosensitivity. Exposure of the resist generates acid which migrates within the polymer film to catalyze the thermal deprotection or cross-linking reaction [10,11]. However, the common CAR system has serious post-exposure delay (PED) problems, such as the appearance of T-top and foot profiles caused by air-borne and substrate contamination, and linewidth variation, which hinder the fabrication of nanometer-scale patterns [12,13]. To overcome the problems of the CAR system, non-chemically amplified resist (non-CAR) systems have been proposed as potential solutions. But, most photo-active compounds (PACs) in non-CAR systems absorb light strongly in the deep UV region, and they are poorly photobleached. Strong absorption of PACs prevents the deep UV light from reaching the bottom of the resist film, leading to very low photosensitivity [14–16].

Single layer resists have been widely used in photolithography. However, the resists should meet the contradictory requirements. Whereas a thin resist film is desired for achieving high resolution, a thick film is better suited for an etch mask [17]. To overcome these limitations, bilayer resists and multilayer resists have been developed, consisting of a thin top imaging layer and a thick underlying layer. Although these systems have a process complexity due to the multiple coating steps, they provide a solution for the formation of high resolution, etch-resistant, and high aspect ratio pattern profiles [18–24].

The top surface imaging (TSI) approach offers a higher resolution than the conventional photolithography

* Corresponding author. Tel.: +82 42 350 2837; fax: +82 42 350 2810.
E-mail address: jbkim21@kaist.ac.kr (J.-B. Kim).

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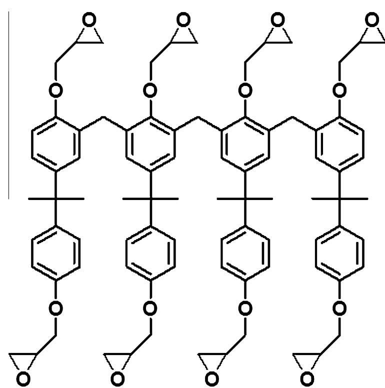

Fig. 1. Chemical stucture of SU-8 #25.

because of the anisotropic pattern transfer of a thin silicon-containing top layer into the thick underlying polymer film. Despite all those advantages of TSI, controlling of the silylation reaction, which is the key process in TSI, on the specific region is still challenged. The insufficient reaction of silicon-containing moieties causes problems with the edge and surface roughness after dry etching. The silylation reaction also changes the molecular weight and volume of the polymer substantially. The swelling results in image distortion [25–27].

In this report we propose a new imaging method combining an interfacial reaction with the multilayer resist system. The aim of this work is to produce high resolution and high aspect ratio patterns by controlling the penetration depth of acid and the anisotropic reactive ion etching (RIE) process. The novel photoresist system is composed of a top acid-labile silicon-containing polymer, an intermediate layer containing a photoacid generator (PAG), and a cross-linked bottom layer. Upon patternwise exposure to UV light, acid is produced in exposed areas of the intermediate layer. The acid diffuses into the top layer during the post-exposure bake and induces cross-linking of the silicon-containing polymer. After development of the top layer, the pattern is transferred into the bottom layer through an oxygen RIE. In this system, PED problems of CAR systems can be solved. The top and bottom layers prevent penetration of basic compounds from the air or substrate and therefore eliminate the T-top or foot. Also problems of top surface imaging might be solved. Silylation induces the swelling problem in the top surface imaging process. In this approach, the silylation process is not necessary.

2. Experimental part

2.1. Materials and instrumentation

Cyclopentanone (98%), Tetrahydrofuran, diethyl ether, toluene, styrene, *tert*-butyl methacrylate (*t*BA), glycidyl methacrylate (GMA), 3-(trimethoxysilyl)propyl methacrylate (TMSPMA), and triphenylsulfonium triflate (TPSTf) were purchased from the Aldrich Chemical Company and used without further purification. Tetrahydrofuran was freshly distilled from sodium/benzophenone (deep purple color) after refluxing for at least 12 h. γ-Butyrolactonyl methacrylate (GBLMA) was purchased from the ENF Technology Company. SU-8 #25 (negative tone photoresist, Fig. 1) was obtained from the MicroChem Corporation. 2,2′-Azobisisobutyronitrile (AIBN) was purchased from the Junsei Chemical Company and purified by recrystallization in methanol. ^{1}H NMR spectra were recorded on a Bruker AM-300 MHz FT-NMR spectrometer in $CDCl_3$ at room temperature. ^{13}C NMR spectrum was recorded on a Bruker AVANCE 400 (inverse gated decoupling mode) in $CDCl_3$ at room temperature. Gel permeation chromatography (GPC) was performed in tetrahydrofuran on a Viscotek T60A GPC system equipped with two PLgel 10 μm MIXED-B columns and a PLgel 10 μm 500A at 35 °C, calibrated with polystyrene standards. The resist film thickness was measured with an Alpha-Step 500 Profiler (Tencor Instrument). Ultraviolet spectra were recorded as spin-coated films on quartz plates with a spectrophotometer (Hewlett–Packard, model 8453). A Headway photoresist spinner was used to apply photoresist solutions on silicon wafers. UV light irradiation was carried out in contact printing mode using a deep UV exposure system (Oriel Corporation, model 82531) with a filter transmitting light between 220 and 260 nm. Scanning electron micrograph (SEM) images were recorded on a Hitachi model S-2280N SEM.

2.2. Polymerization of polystyrene-co-poly(3-(trimethoxysilyl)propyl methacrylate) (PS-co-PTMSPMA)

Styrene (0.78 g, 7.5 mmol) was added to a solution of TMSPMA (4.55 g, 17.5 mmol) and 5 mol% AIBN (0.21 g, 1.25 mmol) in tetrahydrofuran (30 mL) at 65 °C for 24 h in sealed ampoules. After polymerization, solutions of PS-co-PTMSPMA were precipitated into diethyl ether. The precipitated polymers were collected by filtration and washed with the precipitating solvent. After drying under vacuum for 24 h, a white powder was obtained.

^{1}H NMR ($CDCl_3$): δ (ppm) = 0.56–0.64 (m, 9H), 1.57–1.66 (m, 2H), 3.54 (s, 9H), 3.84–4.10 (m, 2H), 6.93–7.24 (m, 10H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 9.81, 13.1, 50.3, 67.9, 126.4, 129.7, 174.2, 177.8.

2.3. Polymerization of poly(tert-butyl methacrylate)-co-poly(glycidyl methacrylate)-co- poly(γ-butyrolactonyl methacrylate) (PtBA-co-PGMA-co-PGBLMA)

*t*BA (1.71 g, 12 mmol), GMA (1.71 g, 12 mmol), GBLMA (1.02 g, 6 mmol), and 5 mol% AIBN (0.25 g, 1.5 mmol) were dissolved in tetrahydrofuran (25 mL). The resulting mixture was heated at 65 °C for 24 h in sealed ampoules. After polymerization, the solution of P*t*BA-co-PGMA-co-PGBLMA was precipitated in diethyl ether. The precipitated polymers were collected by filtration and washed with the precipitating solvent. After drying under vacuum for 24 h, a white powder was obtained.

^{1}H NMR ($CDCl_3$): δ (ppm) = 1.38 (s, 9H), 2.29–2.60 (m, 2H), 3.21 (s, 1H), 4.26–4.43 (m, 2H), 5.33 (m, 1H). ^{13}C NMR ($CDCl_3$): δ (ppm) = 19.1, 21.9, 22.9, 28.7, 44.3, 48.5, 67.6, 77.3, 80.8, 171.9, 177.2.

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