Synthesis of Photosensitive Main Chain Cage Silsesquioxane Polymer

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A novel photosensitive polymer with main chain polyhedral origomeric silsesquioxane (POSS) was synthesized using hydrosilylation polymerization of dihydrosilane POSS and tetrahydropyranyl (THP) group containing di-yne derivatives and subsequent deprotection reaction. The obtained polymer was applied as a negative-working photoresist system with 4,4'-methylenebis[2,6-bis(hydroxymethyl)] phenol as the acid crosslinker and (5-propylsulfonyloxyimino-5*H*-thiophene-2-ylidene)-(2-methylphenyl)acetonitrile as the photoacid generator under 436 nm light and 2.38 wt% tetramethylammonium hydroxide aqueous solution/2-propanol (50:50, v/v). Under optimized condition, the three component resist system was able to generate sharp, 4 μm line patterns and the sensitivity characteristic curve indicate its sensitivity ($D_{0.5}$) and contrast ($\gamma_{0.5}$) are 31 mJ/cm² and 3.1, respectively. Patterned film was crosslinked by thermal treatment at 300 °C and cured film shows enhancement of thermal stability such as 410 °C of thermal decomposition temperature (T_{ds}) and above 300 °C of glass transition temperature (T_g). Furthermore, cured film indicates 2.77 of dielectric constant fairly same as matrix polymer of 2.78.

Keywords: polyhedral origomeric silsesquioxane (POSS), photosensitive, chemically amplified resist

1. Introduction

Contentious miniaturization and integration of very large scale integrated circuits (VLSI) provides higher memory capacity and faster computer processing speeds. The miniaturization of device size induces an increase in the line-to-line capacitance of metal lines, result in resistance-capacitance (RC) delay that limits chip performance. To overcome this problem, developing dielectric interconnects with low dielectric constant is an effective solution [1]. Among these insulation materials, photosensitive polyimides (PSPIs) are promising candidates due to their thermal stability and low dielectric constant. Furthermore, these polymers simplify manufacturing steps because desired patterns can be obtained without any photoresist layer and

subsequent etching process [2]. For these reasons, PSPIs have been widely studied to improve their properties and processabilities [3,4]. However, the high polarization of the imide groups increases the dielectric constant of polymers [5], development of a photosensitive, thermally stable polymer with a lower polarization of the main chain is required.

In previous studies, we synthesized a novel main chain polyhedral origomeric silsesquioxane (POSS) polymer that exhibited high thermal stability and low dielectric constant [6]. These polymers were easily prepared by hydrosilylation polymerization of di-yne derivatives with POSS: Double-Decker-Shaped POSS (DDSQ). The POSS cage structure with large free volume decreases the dielectric constant and imparts thermal stability to the polymers.

In this study, we synthesized novel

photosensitive polymer with main chain POSS polymer with good thermal stability and low dielectric constant. Photosensitivity was easily imparted by attaching a phenolic hydroxyl group as a side chain and photolithographic pattern was developed using 4,4'-methylenebis[2,6-bis(hydroxylmetnyl)] phenol (MBHP) as a crosslinker and (5-propylsulfonyloxyimino-5*H*-thiophen-2-ylidene)-(2-methylphenyl)acetonitrile (PTMA) as the photo acid generator. This three component resist employs a chemically amplified system to achieve good sensitivity. Therefore, thermal cure of patterned film was performed after exposure and development to improve their thermal stability and decreased dielectric constant.

2. Experimental Section

2.1. Materials

DDSQ was kindly donated from Chisso petrochemical Co. Ltd. and used after recrystallization from toluene/acetonitrile. 1,4-bis((4-(tetrahydropyranyloxy)phenyl)ethynyl) benzene (**1**) was synthesized using conventional Sonogashira coupling reaction of *p*-diiodobenzene with 2 equiv. of 4-tetrahydropyranyl ethynylbenzene. Platinum (0) 1,3-divinyl-1,1,3,3,-tetramethyldisiloxane complex (Pt(dvs)) 0.1 M solution in xylene was purchased from Aldrich. Toluene was distilled with sodium. PTMA was kindly donated by Ciba Specialty Chemicals K.K., and used without further purification. MBHP was prepared according to reported procedures [7]. The other reagents and solvents were obtained commercially and used as received.

2.2. Synthesis of Polymer 2

To a 50 mL schlenk bottle DDSQ (2.23 g, 1.99 mmol) and **1** (0.957 g, 2.00 mmol) were added. After argon gas displacement, toluene (4 mL) was added and heated to 100 °C. Then, Pt(dvs) (40 μ L) was added and stirred for 7 h. Toluene (15 mL) was added the reaction mixture and reprecipitated by dropwise addition to 250 mL of vigorously stirred methanol to give a slightly yellow polymer **2** (3.16 g, yield: 97%). $M_n = 19200$, $M_w = 67400$, $M_w/M_n = 3.51$, ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) 7.63-6.27 (m, 54H), 5.30-5.15 (br, 2H), 3.80 (br, 2H), 3.49 (br, 2H), 1.92-1.53 (m, 12H), 0.41-0.22 (m, 6H).

2.3. Synthesis of Polymer 3

To a 500 mL round bottom flask, **2** (3.161 g,

1.94 mmol), THF (340 mL) and 0.1 N HCl aqueous solution (60 mL) were added, then stirred at 50 °C for 12 h. The reaction mixture was then added to NaHCO_3 aq. and washed with brine. The extracts were dried over MgSO_4 , filtered, and concentrated *in vacuo*. The crude product was reprecipitated from THF to $\text{H}_2\text{O}/\text{MeOH}$ (20:1, v/v) to give a slightly yellow polymer **3** (2.53 g, yield: 89%). $M_n = 17700$, $M_w = 58600$, $M_w/M_n = 3.31$, ^1H NMR (CDCl_3 , 300 MHz): δ (ppm) 9.58 (br, 1H), 9.31 (br, 1H), 7.57-6.36 (m, 54H), 0.42-0.19 (m, 6H).

2.4. Dissolution Rate

A 20 wt% solution of polymer **3** containing photo acid generator (PTMA) and crosslinker (MBHP) in NMP was filtered through a syringe filter. The polymer film was spin-coated onto a silicon wafer, prebaked at 100 °C for 2 min, then exposed to a filtered super-high pressure mercury lamp (436nm). After the subsequent post exposure bake (PEB), the film was developed with an aqueous 2.38 wt% tetramethylammonium hydroxide solution (TMAH aq.)/2-propanol (1:1, v/v). The thickness changes of films between before and after development were measured using a Dektak³ surface profiler (Veeco Instrument. Inc.).

2.5. Photosensitivity

A 1.0 μm -thick polymer film on silicon wafer was exposed to 436 nm radiation from a filtered super high-pressure mercury lamp, developed with a 2.38 wt% THAHaq/2-propanol (1:1, v/v) and rinsed with water. A characteristic curve was obtained by the plotting the normalized film thickness as a function of the exposure energy.

3. Results and Discussion

3.1. Polymer Synthesis

A tetrahydropyranyl (THP) containing polymer **2** was synthesized by hydrosilylation polymerization with DDSQ and equal amount of **1** in a quantitative yield (Scheme 1). The chemical structure was characterized by NMR and IR spectra. The ^1H NMR spectrum (Figure 1a) shows new peak consistent with vinyl groups with no decomposition of THP groups, and ^{13}C NMR spectrum indicates absent of a triple bond carbon means hydrosilylation polymerization was successfully accomplished. The molecular weight (M_n) of **2** was estimated at 19,200 with a polydispersity index of 3.51 by gel permeation

chromatography (GPC) with THF as an eluent. The GPC chromatogram of **2** has a unimodal distribution even though generated double bonds are possible reaction sites for hydrosilane to make branch and/or crosslink points. These results indicate that the polymer **2** is consistent with the lack of branched and/or crosslinked structure due to steric hindrance around the main chain double bond.

Deprotection of THP groups from **2** was performed with a catalytic amount of hydrochloric acid to yield desired polymer **3**. The chemical structure of **3** was determined using NMR. The ^1H NMR spectrum (Figure 1b) lacks the THP group and new peaks consistent with an OH group appeared. Molecular weight (M_n) of **3** was estimated at 17,700 and chromatogram was unimodal distribution with polydispersity of 3.31 by GPC. In comparison with polymer **2**, molecular weight of **3** was slightly decreased which indicated little or no main chain cleavage had occurred during deprotection with acid.

3.2. Lithographic Evaluation

Lithographic mechanism applied in this study is

Scheme 1. Synthesis of Hydroxyl Containing POSS Polymer **3**

Figure 1. ^1H NMR spectra of (a) polymer **2** (in CDCl_3) and (b) **3** (in $\text{DMSO}-d_6$).

Scheme 2. Mechanism of **3**/MBHP/PTMA Resist System.

illustrated in Scheme 2. For this resist system, the acid generated by exposure of a photoacid generator (PAG) to UV light reacts with the MBHP crosslinker to generate an electrophile. During the post exposure bake (PEB), electrophilic substitution with polymer **3** generated an insoluble crosslinked polymer in the exposed area. To develop sharp micrometer-sized patterns, optimization of the lithographic condition for various MBHP and PAG loadings, developer compositions, exposure wavelengths, and PEB conditions were performed to measure the dissolution rate of the films.

To determine the exposure wavelength and identify a viable PAG, transmission UV-visible spectrum of a $1\ \mu\text{m}$ thick film of polymer **3** was measured. The film shows 70% transmittance at 365 nm (i-line) and transparent at 436 nm (g-line). Therefore, we decided to expose 436 nm light and use PTMA having an absorption band extending to 450 nm, as a PAG.

To better understand the dissolution behavior of the exposed and unexposed areas, the effects of the crosslinker MBHP, PTMA loading, and post exposure bake (PEB) temperature and time on the

Figure 2. Effect of the MBHP loading on the dissolution rate of the film consisting of polymer **3**, MBHP and PTMA (1.5 wt%) with a 2.38 wt% aqueous TMAHq./2-propanol (50:50,v/v) with 436 nm light and a PEB for 5 min.

dissolution rate in a 2.38 wt% TMAHaq./2-propanol were investigated.

First, the dissolution rate of **3** to various compositions of 2.38 wt% TMAHaq./2-propanol were measured. The dissolution rate increased proportional to the 2-propanol amount and the optimal developer was determined to be TMAHaq./2-propanol (50:50,v/v) at a dissolution rate of 1000 A/s.

The MBHP and PTMA loading effect on the dissolution behavior were then investigated. The dissolution contrasts were higher with larger MBHP loading with an optimum at 10 wt% MBHP loading (Figure 2). On the other hand, PTMA loading was minimized to 1.5 wt% since it did not influence dissolution contrast between 5 to 1.5 wt% loading (Figure 3).

Finally, the effect of PEB temperature and time on the dissolution behavior were investigated under optimized MBHP and PTMA loading

Figure 3. Effect of the PTMA loading on the dissolution rate of the film consisting of polymer **3**, MBHP(10 wt%) and PTMA with a 2.38 wt% aqueous TMAHaq./2-propanol (50:50,v/v) with 436 nm light and a PEB for 5 min.

Figure 4. Effect of the PEB temperature on the dissolution rate of the film consisting of polymer **3** (88.5 wt%), MBHP(10 wt%) and PTMA (1.5 wt%) with a 2.38 wt% aqueous TMAHaq./2-propanol (50:50,v/v) with 436 nm light and a PEB for 5 min.

(Figure 4 and 5). From these measurement, insufficient reaction in the exposed area to be crosslinked occurred at lower PEB temperature (below 110 °C), while undesired crosslinking in unexposed area occurred at higher temperature (above 120 °C). According to these results, we determined 115 °C to be the optimum PEB temperature. When the PEB time is less than 4 min, the exposed area is still soluble to developer while the dissolution behavior of the unexposed area didn't change until after 8 min. According to these reason, PEB time was determined to be 5 min.

After these preliminary optimizations, the characteristic sensitivity curve for a 1 μ m thick polymer film consisting of 88.5 wt% of polymer **3**, 10 wt% of MBHP and 1.5 wt% of PTMA is shown in Figure 6. The curve indicates that the sensitivity ($D_{0.5}$) and contrast ($\gamma_{0.5}$) are 31 mJ/cm² and 3.1, respectively. Thus, this three component system using the main chain POSS photosensitive polymer exhibited high sensitivity and good contrast with g-line.

Figure 5. Effect of the PEB time on the dissolution rate of the film consisting of polymer **3** (88.5 wt%), MBHP(10 wt%) and PTMA (1.5 wt%) with a 2.38 wt% aqueous TMAHaq./2-propanol (50:50,v/v) with 436 nm light and a PEB for 5 min.

Figure 6. Characteristic exposure curve of a film consisting of polymer **3** (88.5 wt%), MBHP(10 wt%) and PTMA (1.5 wt%) with a 2.38 wt% aqueous TMAHaq./2-propanol (50:50,v/v) with 436 nm light and a PEB at 115 °C for 5 min.

A scanning electron micrograph (Figure 7) of a contact-printed negative image obtained with **3**/MBHP/PTMA using optimized conditions shows a line-and-space pattern with sharp 4 μm features.

Figure 7. Scanning electron micrograph of negative images contact-printed film obtained from **3**/MBHP/PTMA system.

3.3. Crosslinking Reaction

Patterned **3**/MBHP/PTMA film was crosslinked by thermal treatment at 300 °C for 3 h under nitrogen. This thermal treatment is expected to induce further crosslinking that increase glass transition temperature (T_g) and decrease the dielectric constant due to conversion from polar hydroxymethyl group of MBHP to nonpolar methylene group of crosslinking site. Thermal properties and dielectric constant of the cured films were measured by thermogravimetric analysis (TGA: Seiko Instruments TG/DTA 6000) and differential scanning calorimetry (DSC: Seiko Instruments DSC 6000), and estimated from the refractive index measured by prism copular (Metricon PC-2000), respectively. These results indicate that the cured polymer possesses thermal decomposition temperature (T_{ds}) of 410 °C and T_g was not observed below 300 °C. Furthermore, the

dielectric constant of 2.77 of the cured film decreased in comparison of non-cured film (2.82) and was nearly the same as that of matrix polymer **3** (2.78). These results suggest that crosslinking reaction occurred by the thermal treatment.

4. Conclusion

A main chain POSS photosensitive polymer **3** was prepared by hydrosilylation polymerization of DDSQ with **1** and subsequent hydrolysis of THP groups. The polymer **3** containing MBHP (10 wt%) and PTMA (1.5 wt%) were applied as a chemically amplified negative-working photoresist system and exhibited a sensitivity of 31 mJ/cm² and a contrast of 3.1. The patterned film crosslinked by thermal treatment at 300 °C for 3 h showed good heat stability (410 °C) and high glass transition temperature (> 300 °C). Furthermore, the dielectric constant of cured film of 2.77 was fairly same as that of the matrix polymer **3** of 2.78.

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