Synthesis of Calixresorcinarene Derivatives with Cross-linking units and Evaluation of Lithographic Performance

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We synthesized a cross-linker incorporated tetrac-methyl-calix[4]resorcinarene (C4RA) derivatives. Molecular glass resists based on the C4RA derivatives showed a high sensitivity (20 mJ/cm²), making it possible to fabricate a 4-μm line-and-space pattern under a 365-nm light (i-line) exposure. Furthermore, an 80-nm L/S pattern could be observed by electron-beam exposure.

Keywords: molecular glass resist / chemical amplified resist / calixarene / patterning

1. Introduction

Chemically amplified resists (CARs) have been the workhorse in photolithography. They have allowed an increased degree of integration and decreased power consumption as well as production cost for microelectronics. For modern CARs, it is necessary to simultaneously improve their resolution, sensitivity and line-edge-roughness (LER). However, because of the trade-off relationship between these three parameters, it is difficult to develop the next-generation CARs. For example, a large diffusion length in the lithography process leads to a high sensitivity, but simultaneously leads to an image blur resulting in negative effects on the resolution and LER [1].

Among these three parameters, the LER is the most serious issue because the LER strongly affects the performance of electronic devices [2]. One of the approaches for solving the LER issues is the reduction of the number of components in the resist films in order to prevent phase-separation, which produces defects at the boundaries of the exposed and unexposed areas.

Another approach to decrease the LER is the use of molecular glass resists. They have low molecular weights, well defined structures and a small pixel size [3]. These unique properties prevent defects in the fine pattern at the boundaries of the exposed and unexposed areas. The effect of the molecular weight on the LER has been already reported in the previous paper [4,5], which describes that the molecular glass resists are the leading candidate for next-generation photoresists. However, in general, low molecular photoresists are likely to show a crystalline behavior, poor film-forming properties and low Tg. Among the molecular glass resists, calixarenes (CAs) and calix[4]resorcinarenes (C4RAs), which are cyclic oligomers synthesized from phenols or resorcinols and aldehydes, are the most prominent candidate, because of their high thermal stability and good film-forming property [6]. Especially, Noria obtained by the condensation reaction of resorcinol and 1,5-pentanediol showed clear line and space patterns with resolutions of 26-40 nm by EUV exposure [7]. Also, calixarenes have already shown a sub-10-nm resolution (dot pattern) by electron-beam exposure, which means CAs and CRAs have the potential to produce a high resolution [8,9,10].

In this study, we synthesized a cross-linker (ethyl vinyl ether group; EVE)-incorporated positive-type molecular glass resist (denoted as EVE-C4RA) based on C4RA (Scheme 1) and evaluated its lithographic performance by i-line (365 nm) and electron-beam lithography.

Scheme 1. Chemical structure of EVE-C4RA.

2. Experimental

2.1 Materials

N-Methyl-2-pyrrolidone (NMP) was purified by vacuum distillation. A 0.24 wt% TMAH aqueous
solution was used as a standard developer. (5-Propylsulfonyloxyimino-5H-thiophene-2,5-diyldene)-(2-methylphenyl)acetonitrile (PTMA) was used as photoacid generator. Other reagents and solvents were used as received.

2.2 Synthesis of C4RA
To a solution of resorcinol (25.2 g, 229 mmol) and acetaldehyde (12.2 ml, 218 mol) in the mixture of ethanol and water (82 ml, 1/1 v/v), a 20.6 ml of conc. HCl aqueous solution was added dropwise with ice bath. Then the reaction mixture was stirred at 75 °C for 1 h. After the reaction, 300 ml of water was added and filtrated. The precipitate was recrystallized from the mixture of methanol and water. (73.0 % yield, 21.6 g) $^1$H NMR (300 MHz, DMSO-$d_6$): 1.34 (d, 12H, CH$_3$), 4.44 (q, 4H, CH), 6.15 (s, 4H, aromatic H), 6.85 (s, 4H, aromatic H), 8.47 (s, 8H, –OH). IR (KBr, cm$^{-1}$): 2931, 2873 (v -CH-), 1619, 1508, 1427 (v C=C aromatic).

2.3. Synthesis of EVE-C4RA substituted with 2.7 vinyloxy groups (2.7 sub. EVE-C4RA)
To a solution of sodium hydride (0.360 g , 15.0 mmol) in 14 ml of NMP, C4RA (1.36 g, 2.50 mmol) and tetrabutylammonium bromide (0.08 g, 0.025 mmol) were added and stirred for 10 min. Then chloroethyl vinyl ether (1.52 ml, 15.0 mmol) was added and stirred at 80 ºC for 16 h. After the reaction, 150 ml of a 2.38 wt% TMAH aqueous solution and 50 ml of diethyl ether were added and aqueous layer was separated. The aqueous layer was neutralized with a 5 wt% citric acid aqueous solution and added 50 ml of ethyl acetate. The solution was washed with water three times and dried over MgSO$_4$ to give brown solid. The brown solid was washed with chloroform/hexane mixture twice and dried at 30 ºC in vacuo. Yield: 1.08 g (58.8 %). $^1$H NMR (300 MHz): 1.2 - 1.4 (12H, CH$_3$), 3.3 - 4.5 (20.2 CH, CH=CH$_2$), 6.0 - 7.0 (7.7H, aromatic H, –CH=), 8.3 - 8.7 (2.2H, –OH). IR (KBr, cm$^{-1}$): 2931, 2873 (v -CH-), 1619, 1500 (v C=C aromatic), 1238, (v C-O-C).

2.5. Dissolution rate measurements
The photoresist films with 0.7 µm thickness on a silicon wafer were prepared from a cyclopentanone solution of 2.7 sub. EVE-C4RA (95 wt%) and PTMA (5 wt%). The prepared photoresists were pre-baked (PB) for 3 minutes at various temperature. Then the films were exposed to i-line using filtered super-high-pressure mercury lamp. Imagewise exposure was carried out in a contact-printing mode. The exposed films were post-exposure-baked (PEB) at various time and temperature, followed by developing with a 0.24 wt% TMAH aqueous solution for 30 s. The film thickness was measured with a Dektak surface profiler.

2.6. Measurements of sensitivity curve
The photoresist films with 0.7 µm thickness on a silicon wafer were prepared from a cyclopentanone solution of 2.7 sub. EVE-C4RA (95 wt%) and PTMA (5 wt%). The prepared resist films were exposed to i-line using super-high-pressure mercury lamp with changing an exposure dose after PB (100 ºC, 3 min.). Then the resist film was post-exposure-baked (110 ºC, 1 min.) and developed with 0.24 wt% TMAH aqueous solution. The characteristic sensitivity curve was obtained by the plotting of normalized film thickness to the exposure dose. Imagewise exposure was carried out in a contact-printing mode.

2.7 Fabrication of the fine pattern with electron-beam exposure
The photoresist films with 70 nm thickness on a silicon wafer were prepared from a cyclopentanone solution of 2 wt% EVE-C4RA (2.7-sub.) and triphenylsulfonium-triflate (15 wt%) and trioctylamine (0.3 wt%). The PB temperature, PB time, PEB temperature, PEB time, developer and developing time were 100 ºC, 3 minutes, 80 ºC, 60 s, 0.24 wt% TMAH aqueous solution, and 30 s, respectively. The prepared resist films were exposed to electron-beam (100 keV, 220 μC/cm$^2$).

2.8. Measurements
Fourier-transferred (FT-IR) spectra were recorded on Horiba FT-720. Thermogravimetry (TG) was performed with a Seiko TG/DTA 6300. The film was spin-coated on a silicon wafer from a polymer solution in cyclopentanone, and the film thickness was measured by Veeco Instrument Dektak$^3$ surface profiler. In evaluation with i-line lithography, field emission scanning electron microscopy (SEM) was taken with a Technex Lab Tiny-SEM 1540 with 15kV acceleration voltage for imaging. Pt/Pd was


3. Results and Discussion

3.1 Design of EVE-C4RA

C4RA has a high thermal stability despite its low molecular weight. In addition, it has many advantages, such as a good etching resistance, good adhesion to the Si substrate, synthetic facility, etc. Thus, we designed EVE-C4RA which is a cross-linker incorporated molecular resist based on C4RA. The patterning process with EVE-C4RA is shown in Scheme 2. One of the advantages is prevention of phase-separation in the resist film due to the incorporation of a cross-linker into the resist structure. The cross-linking reaction in an unexposed area also leads to an improved mechanical strength of the formed pattern and inhibits pattern collapse. Furthermore, due to the low activation energy for the cleavage of the acetal by the photo-generated acid, EVE-C4RA would be expected to have a high sensitivity.

3.2 Synthesis and characterization of EVE-C4RA

EVE-C4RA was synthesized from C4RA and chloroethyl vinyl ether in NMP. The average number of EVE groups in EVE-C4RA was determined by the ratio of the methyl protons (1.2 - 1.4 ppm) to the methylene, methine and vinyl ether protons (3.3 - 4.5 ppm) in the 1H-NMR spectrum. When the substitution number is above 2.7, EVE-C4RA became insoluble in a 0.24 wt% TMAH aqueous solution. Thus, in this study, 2.7 sub. EVE-C4RA was used. The thermal stability was measured by thermogravimetry (TG). EVE-C4RA began to decompose around 260 °C under nitrogen.

3.3 Lithographic evaluation

The patterning process of EVE-C4RA is shown in Scheme 1. In this section, the effects of the PB temperature, PEB temperature, PEB time, sensitivity, and patterning behavior were evaluated by using the i-line or electron-beam exposure.

3.3.1 Effect of PB

As shown in Scheme 1, the molecular glass resist based on the 2.7 sub. EVE-C4RA should be cross-linked during the PB, therefore, we first studied the PB effect (Figure 1). The dissolution rates of the resist films to a 0.24 wt% TMAH aqueous solution after the PB at various temperatures were measured. The results are shown in Figure 1. The dissolution rate decreased with an increase in the PB temperature. Especially, the resist films became insoluble after the PB at temperatures above around 80 °C, indicating that an adequate cross-linking reaction took place and the 2.7 sub. EVE-C4RA resist became insoluble in the developer. However, a little swelling was observed at a temperature of 130 °C. Thus, the PB temperature was fixed at 100 °C.

![Figure 1. Effect of PB temperature on the dissolution rate for 2.7 sub. EVE-C4RA resist.](image-url)
in the exposed area increased with the increasing PEB temperature, and the DC between the exposed and unexposed areas reached more than 100 times at temperatures from 90 °C to 120 °C, which means that the cleavage of the cross-linking by acids has effectively occurred at any temperature. However, a little swelling was observed in an unexposed area at 80 °C and 130 °C, and the dissolution rate in the exposed area remarkably decreased at 130 °C. Thus, the PEB was determined at 110 °C for the following evaluations.

Figure 2. Effect of PEB temperature on the dissolution rate for 2.7 sub. EVE-C4RA resist in exposed and unexposed areas.

3.3.3. Effect of PEB time
The effect of the PEB time on the dissolution rate of the EVE-C4RA films was investigated and the results are shown in Figure 3.

The PB time and exposure dose were 3 minutes and 100 mJ/cm², respectively. The dissolution rate in the exposed area increased by increasing the PEB time, especially the dissolution rate in the exposed area was high enough to obtain an adequate DC at PEB times longer than 1 minute. This suggested that the cleavage of the acetal cross-linking effectively proceeded at the PEB temperature of 110 °C and the PEB time of 1 minute.

Figure 3. Effect of PEB temperature on the dissolution rate for 2.7 sub. EVE-C4RA resist in exposed and unexposed areas.

3.3.4 Characteristic photosensitive curve of 2.7 sub. EVE-C4RA resist
The photosensitive curve of the 2.7 sub. EVE-C4RA resist is shown in Figure 4. The film thickness, developer and developing time were 0.7 µm, a 0.24 wt% TMAH aqueous solution, and 30 s, respectively. The resist has the high sensitivity of 20 mJ/cm² and good contrast of 7.8 with i-line exposure.

Figure 4. Characteristic photosensitive curve of 2.7 sub. EVE-C4RA resist.

3.3.5 Pattern formation of 2.7 sub. EVE-C4RA resist by i-line exposure
Figure 5 shows an SEM image of the contact printed image obtained from the 2.7 sub. EVE-C4RA resist. The exposure dose and developer were 30 mJ/cm² and a 0.24 wt% TMAH aqueous solution, respectively. A clear positive pattern with a half-pitch of 4 µm was successfully obtained.
3.4 Pattern formation of 2.7 sub. EVE-C4RA resist by electron-beam exposure

Based on the i-line lithography study, the pattern formation by electron-beam lithography was carried out. In this evaluation, the fine pattern with a half-pitch of 80 nm and the blurred pattern with a half-pitch of 35 nm were observed at a 100 keV electron-beam exposure for the dose of 220 µC/cm² (Figure 6). The LER was calculated from the 80-nm line-and-space pattern to be 7.5 nm which is higher than the target value. Further optimization is required for a higher resolution and lower LER.

4. Conclusion

The molecular resist based on the 2.7 sub. EVE-C4RA showed a high sensitivity (20 mJ/cm²) and high resolution (4-µm half-pitch pattern) with i-line exposure. The fine pattern with a half-pitch of 80 nm was obtained by electron-beam exposure. However, the LER was the high value of 7.5 nm. Further optimization is required to obtain a sub-50-nm half-pitch pattern and lower LER.

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Reference