HIGHLY SENSITIVE ELECTRON-BEAM NEGATIVE RESISTS UTILIZING PHENYLCARBINOL AS DISSOLUTION-INHIBITOR PRECURSOR


Central Research Laboratory, Hitachi, Ltd., Kokubunji, Tokyo 185, Japan
*Hitachi Research Laboratory, Hitachi, Ltd., Hitachi, Ibaraki 319 12, Japan
**Yamazaki Works, Hitachi Chemical Co., Hitachi, Ibaraki 317, Japan

Chemically amplified negative resists made by utilizing the polarity-change reaction of phenylcarbinol were investigated for electron beam lithography. The resist composed of 1,3-bis(α-hydroxyisopropyl)benzene (Diol-1), m/p-cresol novolak resin, and diphenyliodonium trifluoromethanesulfonate (DITf) showed the best lithographic performance in terms of sensitivity and contrast among the resists using phenylcarbinol. Fine 0.25-μm line-and-space patterns were formed by using this Diol-1 resist with a dose of 3.6 μC/cm² in conjunction with a 50-kV electron beam exposure system.

1. Introduction

Electron beam lithography is one of the most promising microlithographic techniques to take over from optical lithography, and has already been used to fabricate photomasks and customized LSIs. However, there are several problems to be solved before electron beam lithography becomes practical as a lithographic tool for the next generation of device fabrication methods. One of the main problems is low throughput. Although electron beam exposure systems equipped with cell projection have recently been proposed to improve the throughput [1,2], highly sensitive resists still needed to be developed to further improve it.

The best approach for developing a highly sensitive resist is chemical amplification [3]. Chemically amplified negative resists made by utilizing the crosslinking reaction of amino resins have been widely used in both optical and electron beam lithography [4,5]. Another system of chemical amplification negative resists is made by utilizing the polarity-change reactions responsible for the resists insolubilization mechanism [6-13]. They consist of a polymer matrix, an acid generator, and a dissolution inhibition precursor (DIP) that can be converted into a dissolution inhibitor by an acid-catalyzed reaction. In this paper, acid-catalyzed intramolecular dehydration of
phenylcarbinols is used to design highly sensitive negative resists suitable for electron beam lithography.

2. Method

1,3-Bis(α-hydroxyisopropyl)benzene (Diol-1), and 1,4-bis(α-hydroxyisopropyl)benzene (Diol-2) were purchased from Tokyo Chemical Industry Co., and hydrobenzoin (HB) from the Aldrich Co., and all three were used without further purification. Hexa(methoxymethyl)melamine (HMM) with the tradename Cymel 300 was purchased from Mitsui Cyanamid Co., and was used after elimination of metal ion impurities by column chromatography. m/p-Cresol novolak resin was supplied by Hitachi Chemical Co. Diphenyliodonium trifluoromethanesulfonate (DITf), diphenyliodonium p-toluenesulfonate (DITs), diphenyliodonium naphthylsulfonate (DIN), diphenyliodonium hexafluoroantimonate (DIA), and diphenyliodonium chloride (DICl) were synthesized by an established method [14]. An aqueous base developer, 2.38-wt% tetramethylammonium hydroxide with the tradename NMD-3, was purchased from Tokyo Ohka Kogyo Co.

A resist solution was prepared by dissolving a dissolution-inhibitor precursor (DIP) and an onium salt in 20-wt% novolak resin cyclohexanone solution. The weight ratio of the resist components was varied as follows: novolak resin/DIP/DIT=100/5–40/0.5–3. The resist solution was spun onto a Si wafer and baked on a hotplate at 80°C for 2 minutes to obtain a 1-µm-thick resist film. The lithographic performance parameters, i.e., sensitivity and contrast, were evaluated from sensitivity curves obtained by plotting the normalized film thickness as a function of the exposure dose. The film thickness was determined with an Alpha-step 200 (Tencor Instrument Co.) profilometer. The dissolution rates were determined by measuring the time to dissolve the resist films in the aqueous base developer. To measure the resist sensitivity, a modified SEM (Hitachi S-570) with a 30-kV acceleration voltage was used. To evaluate lithographic resolution, a Hitachi HL-750 with a 50-kV acceleration voltage was used. After EB exposure and subsequent baking (80°C for 2 minutes), the resist films were developed in the developer. The diffusion ranges of acids generated from onium salts were measured by using the same method as reported by L. Schlegel, et al. [15].

3. Results and Discussion

The sensitivity and contrast of resists using three phenylcarbinols as DIPs were compared with those of a resist using HMM as a crosslinker (Fig. 1). The weight ratio of the novolak resin/DIP/DITf was kept constant (100/20/2). As can be seen in Fig. 1, the resists using
phenylcarbinols show higher sensitivity than the resist using HMM under the same baking conditions. Since the Diol-1 resist showed the highest sensitivity and contrast, Diol-1 was selected as the DIP for a highly sensitive EB resist system.

The effect of the Diol-1 concentration on the resist sensitivity and contrast is shown in Fig. 2. In this experiment, the Diol-1 concentration was varied while the weight ratio of novolak resin to DITf was kept constant at 100/2. The sensitivity became higher as the Diol-1 concentration was increased, and the contrast reaches a maximum at a 20–30-wt% Diol-1 concentration.

The sensitivity curves of resists with different diphenyliodonium salts are shown in Fig. 3. The weight ratio of the novolak/Diol-1/onium salt was kept constant (100/20/2). The resists using DITf, DITs, DIN, and DIA exhibited about the same sensitivity and contrast while the resist using DICI had lower sensitivity and contrast. Large film thickness loss was observed in the sensitivity curve of the DICI resist. The molecular weight of the acid produced from DICI was one order of magnitude smaller than those of acids produced from the other onium salts. Therefore, the acid produced from DICI probably has long-range diffusion and a high evaporation coefficient.

To investigate the diffusion characteristics of the acids produced from onium salts, diffusion range was measured using the method shown in Fig. 4. The film consisting of novolak, Diol-1, and an onium salt was coated onto a silicon wafer. After baking, the film was flood-exposed to deep-UV light to generate a large amount of acid. A thick film containing Diol-1 and novolak was coated onto an aluminum foil and baked at 100°C for 2 minutes. The film was then peeled from the aluminum foil and pressed onto the flood exposed film. The composite film was baked at 100°C for
15 to 300 minutes. The regions of the film into which acid had diffused became insoluble and remained after the base development process. The diffusion range of the acid was estimated from the remaining film thickness.

The film thickness is plotted as a function of baking time (sec) in Fig. 5. The diffusion of toluenesulfonic acid and naphthalenesulfonic acid occurred in a very short period of time while trifluoromethanesulfonic acid and hexafluoroantimonic acid diffused gradually. These results indicate that the molecular size of the acid is not the dominant factor controlling the diffusion range in the Diol-1 resist system. The acid strength is probably responsible in the case of Diol-1 resist, because trifluoromethanesulfonic acid and hexafluoroantimonic acid are much more acidic than toluenesulfonic acid and naphthalenesulfonic acid. At lower temperature (70°C, not shown), trifluoromethanesulfonic acid hardly moves in the resist film, and no film remained even after 300 sec of baking. Since the acid produced from DITf had a relatively small diffusion range among theonium salts investigated here, and moreover DITf does not contain any metallic ions, DITf was selected as the acid generator for the Diol-1 resist.

The dependence of the resist sensitivity on the DITf concentration is shown in Fig. 6. The weight ratio of novolak resin to Diol-1 was kept constant at 100/20, while the DITf concentration was varied. The resist film was prebaked at 90°C for 2 minutes and post-exposure baking was carried out at 70°C for 2 minutes. The sensitivity increased with the DITf concentration, and the dissolution rate of the unexposed film decreased with the DITf concentration because DITf acts as a dissolution inhibitor of
novolak resin [16]. The DITf concentration needs to be optimized to make the best use of the Diol-1 resist in terms of sensitivity and development time.

Patterning of a resist composed of novolak resin, Diol-1, and DITf (a weight ratio of 100/20/0.5) was carried out with an EB lithography system (Hitachi: HL-750, 50 kV). The resist film was prebaked at 100°C for 2 minutes and post-exposure baking was carried out at 70°C for 2 minutes. A 0.25-µm line-and-space pattern was resolved for a 1-µm-thick resist with a dose of 3.6 µC/cm² (Fig. 7).

Fig. 5. Diffusion range of acids generated from onium salts by exposure to deep-UV light (wavelength: 248 nm)
Baking Temperature: 100°C

Fig. 6. Effect of DITf concentration on resist sensitivity. Novolak resin/Diol-1/DITf=100/20/y (weight ratio)

Fig. 7. SEM microphotograph showing 0.25-µm L/S patterns delineated using EB exposure (acceleration voltage: 50 kV) of the resist using Diol-1 as its DIP.
Dose: 3.6µC/cm²
PB: 100°C/2 min, PEB: 70°C/2 min
4. Conclusion

We have developed chemical amplification resists using phenylcarbinols as dissolution-inhibition precursors for electron beam lithography. Among the phenylcarbinols investigated here, 1,3-bis(α-hydroxyisopropyl)benzene (Diol-1) provides the best lithographic performance in terms of resist sensitivity and contrast. Applying the resist containing Diol-1 to electron beam lithography, 0.25-μm line-and-space patterns were delineated with a dose of 3.6 μC/cm² in conjunction with a 50-kV electron beam exposure system.

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