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Novel electron beam resist material using hydrophilic protecting group

Satoshi Saito [a,*], Tetsuro Nakasugi [b]

[a] Corporate Research and Development Center, Toshiba Corporation, 1, Komukai Toshiba-cho, Saiwai-ku, Kawasaki, Japan
[b] Process and Manufacturing Engineering Center, Semiconductor Company, Toshiba Corporation 8, Shinsugita-cho, Isogo-ku, Yokohama, Japan

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Abstract

We discuss a new EB resist material that has an alicyclic (bulky) acetal protecting group, with a hydrophilic group in its chemical structure. We synthesized it by acid catalyzed reaction of poly(hydroxystyrene, PHS) with hyper lactonyl adamantyl vinyl ether (HPVE). AFM analysis showed that the resist composed of HPVE polymer exhibits a uniform dissolution property. And the etching durability was double that of poly(methyl methacrylate) and better than that of ethoxy ethyl-protected PHS. EB resist composed of this material provides 60 nm-L/S patterns at less than 8 μC/cm^2 with a 50 kV EB exposure system.

Keywords: EB lithography; Resist; Acetal; Alicyclic; Adamantane; Lactone; Solubility parameter

1. Introduction

Electron beam (EB) lithography is the most promising technology for the fabrication of future-generation devices which need nanometer-scale dimensions, due to its high-resolution capability [1]. It is well known that one of the serious issues for EB lithography is the poor throughput. To solve this problem, it is necessary for EB resist materials to have high-resolution and high-sensitivity capabilities. Although many EB resist materials have been reported [2–5], not all of them have both high-resolution and high-sensitivity capabilities. We have already reported that, for high resolution and low line-edge roughness (LER), lower M_w and narrow distribution of base polymer are important [6]. We describe a new EB resist material that has an acetal bulky protecting group containing a hydrophilic group and present the results for lithographic performances.

* Corresponding author.
E-mail address: sat-saito@mdl.rdc.toshiba.co.jp (S. Saito).

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2. Experimental

2.1. Material

Poly(hydroxystyrene) (PHS), with M_w (4000) and M_w/M_n (1.1), is used for base polymer. Adamantyl vinyl ether (AVE) and hyper lactonyl adamantyl vinyl ether (HPVE) were supplied from Daicel Chemical's laboratory. Ethyl vinyl ether was purchased from Wako Pure Chemical Industries, Ltd. PHS partially protected with these acetal groups was synthesized in ethyl acetate solution by acid catalyzed reaction of PHS with vinyl ether in our laboratory. Satisfactory synthesis was carried out using dichloro acetic acid as a catalyst. Naphthalimidyl camphorsulfonate (Midori Kagaku Co.) was used as photo-acid generator. The ratio of the photo-acid generator to the polymer was 5 wt%.

2.2. AFM

The surface roughness of each resist film on Si wafer was measured using a Nanoscope 3100 atomic force microscope (Digital Instrument) under tapping mode. All samples were spin-coated on Si wafers and baked at 110 °C. After controlled tetramethylammonium hydroxide (TMAH) alkaline development for 30, 60 and 120 s, nm-scale surface roughness appeared on the resist films. Afterwards, AFM images of surface of resist films were measured and the surface roughness was obtained using AFM software.

2.3. Resist evaluation

EB exposure was carried out by using a Hitachi HL-900D direct writing system at 50 kV. After EB exposure, post-exposure bake was carried out for 90 s at 100 °C. The samples were then developed using a 1.19 wt% TMAH alkaline developer. The etching durability was measured using a DEM-451 (ANELVA) plasma dry etching system. The etching conditions were 10-mTorr CF_4 gas and 100-W power.

3. Results and discussions

3.1. Dissolution properties

Fig. 1 shows the chemical structures of base polymer (PHS) and protecting groups. It is well known that AVE is the typical hydrophobic protecting group. On the other hand, HPVE is expected to have a hydrophilic property due to the introduction of lactonyl group (polar group) into adamantane backbone. Fig. 2 shows the relationship between the protecting ratio and the dissolution rate. As a reference, the dissolution rate for conventional alkyl-type protecting group (ethoxy ethyl group (ETE)), synthesized by ethyl vinyl ether, is also shown in Fig. 2. It shows that the HPVE has weaker inhibition capability compared to AVE and similar capability to ETE.

One of the effective parameters for predicting hydrophilicity is a solubility parameter δ ($cal^{0.5}/cm^{1.5}$). According to the literature [7,8], the δ for these vinyl ethers can be estimated. The value of δ for AVE is 5.79, HPVE is 7.36 and ETE is 7.29. Lower δ means lower hydrophilicity. These values suggest that the hydrophilicity of HPVE is almost the same as that of ETE and higher than that of AVE. The results for dissolution properties of these polymers are in good agreement with the estimated values. Additionally, Fig. 2 showed that protection ratios of about 25% for HPVE and 20% for AVE seem to be required for resist material to maintain good dissolution contrast between unexposed area and exposed area.

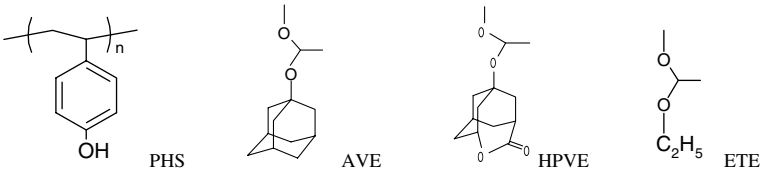

Fig. 1. Chemical structures of base polymer and protecting groups.