Study on Organosilicon Positive Resist. III. Organosilicon Positive Excimer Laser Resist (OSPR-2016)

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SYNOPSIS

A new alkali-developable organosilicon positive excimer laser (KrF) resist (OSPR-2016) has been developed for a bilayer resist system. OSPR-2016 is composed of poly(*p*-hydroxybenzylsilsesquioxane) and methyl cholate-tris(α-diazoacetoacetate). The ratio is 72.5 : 27.5 w/w. A sample of 0.5-μm thick OSPR-2016 resolved 0.35 μm L&S patterns when exposed to a dose of 320 mJ/cm^2 from an excimer laser projection printer (NA = 0.37).

INTRODUCTION

A variety of high resolution lithography techniques has been needed for achieving higher density circuits in microelectronic devices. Difficulties are currently present in resolving below half-micron patterns on a nonplanar device surface. A bilayer resist system using organosilicon resist has become more and more important because it overcomes the difficulties in patterning on the surface of a nonplanar device.[1] It was also anticipated that KrF excimer laser lithography would be a tool capable of resolving fine patterns below a half-micron.[2] The recently reported OSPR-1334, however, was not suitable for excimer lasers because it was designed for an i–g line, has a high initial absorption, and does not bleach efficiently in the deep UV region. Consequently, it could produce sloping pattern profiles when exposed to an excimer laser and we decided to develop a new organosilicon resist for use in excimer laser lithography.

Various types of photoactive compounds (dissolution inhibitors) have been proposed for the excimer laser. Willson et al.,[3,4] Scwartzkopf,[5] and Tani et al.,[6] reported on diazodiketone compounds, and Reichmanis et al. described *o*-nitrobenzyl cholate systems.[7,8] We have already reported that methyl cholate-tris(α-diazoacetoacetate) (**1**, shown in Scheme 1) is the most effective photoactive compound among the novel α-diazoacetoacetates derived from steroids and aliphatic polyfunctional alcohols which we prepared. An admixture of **1** with poly(*p*-hydroxybenzylsilsesquioxane) (**2**, shown in Scheme 2) gives a new alkali-developable organosilicon positive excimer laser resist.[9] In this paper we present the characteristics of the above-mentioned new resist in detail.

EXPERIMENTAL

Materials

Methyl cholate-tris(α-diazoacetoacetate) (**1**) and poly(*p*-hydroxybenzylsilsesquioxane) (**2**, M_w = 3300, M_w/M_n = 1.2, OH-conversion = 88%) were used as the photoactive compound and the matrix resin, respectively. The preparative methods and the properties have already been reported.[9] 1-Acetoxy-2-ethoxyethane was used as the resist solvent. An organic alkali, tetrakis(2-hydroxyethyl)ammonium hydroxide, was adopted as the developer. BLOC (Hitachi Chemical Co.) was employed as a bottom layer of the bilayer resist system.

Lithographic Procedure

The typical lithographic procedure is as follows. Resist solutions, of which the solid concentrations were adjusted to form a 0.5-μm-thick layer, were spin-coated on silicon wafers which had been previously coated with a 1.7-μm-thick BLOC, and were prebaked for 30 min at 90°C. The samples were exposed

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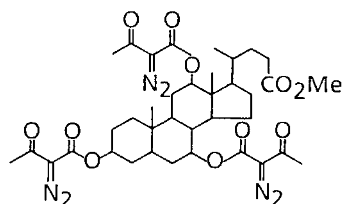


Scheme 1 Molecular structure of methyl cholate-tris(α-diazoacetoacetate) (1).

to deep UV with a 500W Xe-Hg arc lamp and the exposed resists were immersed in the developer for 1 min at 25°C. The deep UV intensity was measured at 254 nm using an irradiance tester (Ushio Electric UIT-200). The bleaching abilities of the resists on quartz were measured by a Hitachi 200-10 UV spectrometer. The imaging test was performed with a Canon FPR-4500 Fine Pattern Aligner (NA = 0.37).

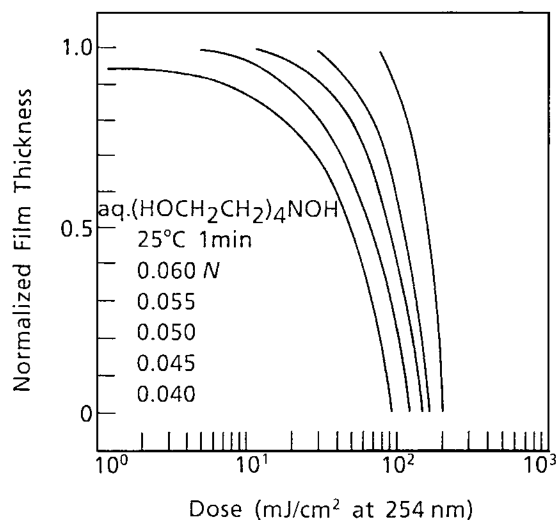
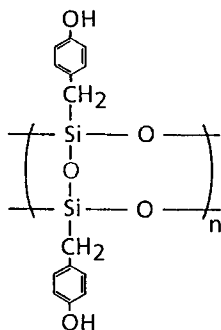


Figure 1 Exposure (Xe-Hg) characteristics of 0.5 μm-thick resist (2 : 1 = 80 : 20 w/w) in which the developer concentrations are varied.

RESULTS AND DISCUSSION

Resist Components

We previously prepared and reported on novel α-diazoacetoacetates derived from steroids and simple polyfunctional alcohols which undergo photolysis to give carboxylic acids and exhibit excellent bleaching effects.[9] The steroid systems are superior to the nonsteroid systems in dissolution inhibiting ability. In the steroid resist system, the resist sensitivities increase with the increasing number of photoactive groups in one photoactive molecule, but level off when the number of photoactive groups reaches three, although this number should be reduced to achieve suitable transparency. We selected methyl cholate-tris(α-diazoacetoacetate) (**1**) as the best photoactive compound among the α-diazoacetoacetates we prepared. Compound **1** has an effective bleaching ability at 248 nm; the initial molecular extinction coefficient of 1.88×10^4 is reduced to 0.35 $\times 10^4$ by exposure, and the dissolution inhibiting ability is almost the same as that of *o*-naphthoquinone diazide for poly(*p*-hydroxybenzylsilsesquioxane) (**2**). The composite prepared from **1** and **2** became the KrF excimer laser resist. Compound **2** has already been mentioned in advance of this study, and has a high transmittance (73%) at 248 nm. We optimized the developer concentration and the resist composition ratio to obtain the highest resolution.



Scheme 2 Molecular structure of poly(*p*-hydroxy-benzylsilsesquioxane) (2).

Developer

Exposure (Xe-Hg) characteristics of 0.5-μm-thick resist (2 : 1 = 80 : 20 w/w) are shown in Figure 1 in which the developer concentrations are varied. It was mentioned in the previous paper that aqeous $(HOCH_2CH_2)_4NOH$ was a suitable developer for **2**. As the concentration decreases, the γ value increases, although the sensitivity decreases. The lowest concentration which could be used was 0.040*N*. In the case of 0.035*N*, a normal exposure curve was not obtained. This phenomenon was the same in various resist compositions prepared from **2** and **1**. Therefore we fixed the concentration at 0.045*N*, taking into account the developing margin.

Resist Composition

Exposure (Xe-Hg) characteristics of 0.5-μm-thick resist are shown in Figure 2 in which the ratios of

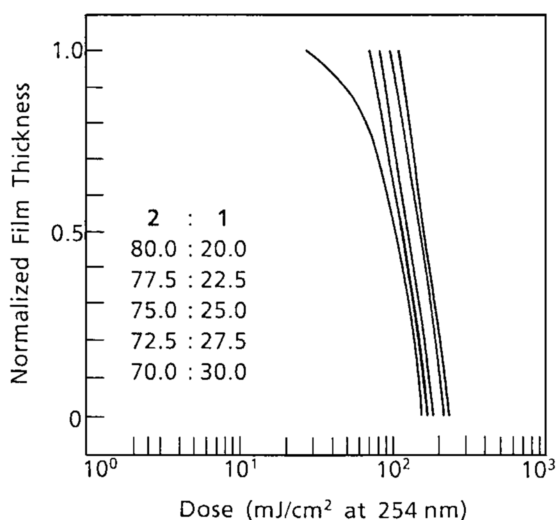


Figure 2 Exposure (Xe-Hg) characteristics of 0.5 μm-thick resists in which the ratios of 2 and 1 are changed, and the developing condition is fixed at 0.045 N aqueous $(HOCH_2CH_2)_4NOH$.

2 and **1** are varied from 80 : 20 to 70 : 30. The γ value is already saturated at about 3 in this range. Moreover the unexposed film remains perfectly, while diminishing of the exposed film occurs suddenly over 22.5 wt % of **1**. However, the sensitivity decreases with increases in the percentage of **1**.

Bleaching abilities of 0.5-μm-thick resists are shown in Figure 3 in which the ratios of **2** and **1** are varied from 80 : 20 to 70 : 30. The initial transmittances at 248 nm are within the range 45% to 25%, and the bleaching abilities improve to some extent with increases in the percentage of **1**, although the transmittances as a whole decrease.

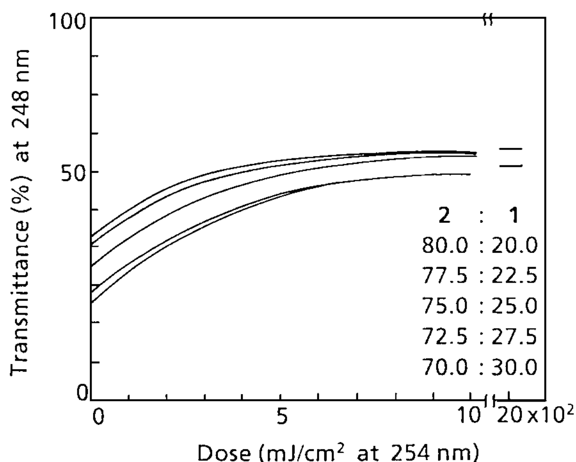


Figure 3 Bleaching abilities of 0.5 μm-thick resists in which the ratios of 2 and 1 are varied.

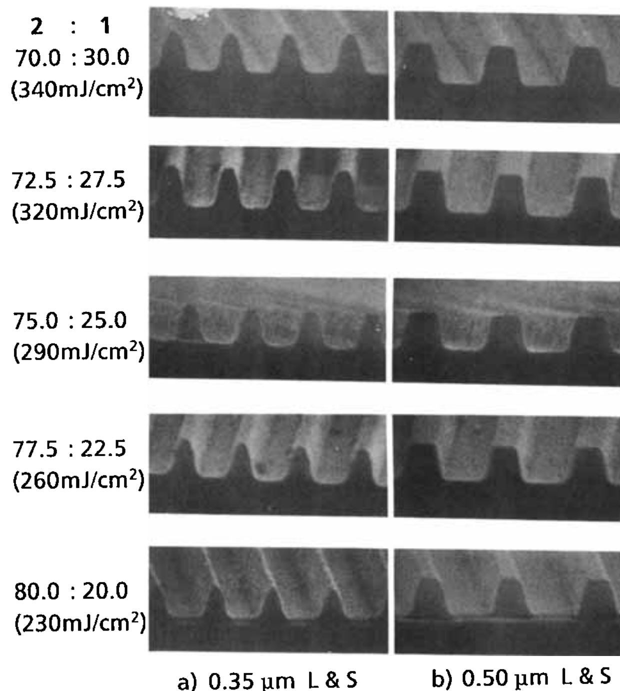


Figure 4 SEM photographs of the 0.35 and 0.50 μm L&S patterns of 0.5 μm-thick resists in which the ratios of 2 and 1 are changed. Doses are in parentheses.

These results might indicate that increases in the percentage of **1** alone could not lead to high resolution because the simultaneous decrease in the

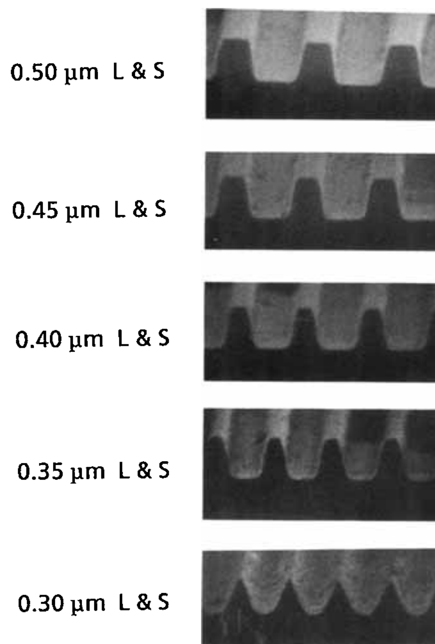


Figure 5 SEM photographs of 0.30- to 0.50-μm L&S patterns of 0.5 μm-thick OSPR-2016.

transmittance is an undesirable factor reducing the resolution. Therefore, we decided to optimize the composition ratio by observing the profiles patterned with the excimer laser stepper.

Figure 4 shows SEM photographs of the 0.35 and 0.50 μm L&S patterns of 0.5-μm-thick resists in which the ratios of **2** and **1** are varied from 80 : 20 to 70 : 30. The resolution improves gradually with increases in the percentage of **1**. The improvement ceases at 27.5 wt % of **1**, however. At this point, the resolution is reduced by the addition of **1**. We determined the optimal resist composition ratio to be **2** : **1** = 72.5 : 27.5 w/w and designated this resist OSPR-2016.

Figure 5 shows SEM photographs of 0.30- to 0.50-μm L&S patterns of 0.5-μm-thick OSPR-2016. The highest resolution is for 0.35-μm L&S patterns and the dose is 320 mJ/cm^2 at 248 nm. This resolution limit could not be changed even if the resist thickness was reduced to 0.35 μm although the dose could be decreased to 260 mJ/cm^2.

CONCLUSIONS

A new alkali-developable organosilicon positive excimer laser resist (OSPR-2016) was developed for the bilayer resist system. OSPR-2016 is composed of poly(*p*-hydroxybenzylsilsesquioxane) and methyl cholate-tris(α-diazoacetoacetate) with the optimized ratio of 72.5 : 27.5 w/w. The highest resolution of 0.5-μm-thick OSPR-2016 is 0.35 μm when exposed to the dose of 320 mJ/cm^2 from an excimer laser projection printer (NA = 0.37) and developed with 0.045*N* aqueous $(HOCH_2CH_2)_4NOH$.

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