

Study on Organosilicon Positive Resist. II. Organosilicon Positive Photoresist (OSPR-1334) and Its Application to Bilayer Resist System

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SYNOPSIS

A new alkali-developable organosilicon positive photoresist (OSPR-1334) and a bilayer resist process with OSPR-1334 has been developed. OSPR-1334 is composed of poly(*p*-hydroxybenzylsilsesquioxane) and naphthoquinone diazide. The sensitivity and the resolution are almost the same as those of conventional novolac-based resists when aqueous tetrakis(2-hydroxyethyl) ammonium hydroxide is used as a developer. Also, OSPR-1334 has excellent resistance to O₂RIE. The etching rate is 3.6 nm/min, while that of polyimide resins or hard-baked novolac-based resists is 100 nm/min. OSPR-1334 is suitable for use as the top layer of the bilayer resist system. OSPR-1334, after O₂RIE, can be eliminated by dissolving an unchanged layer followed by spinning out or filtrating a changed surface layer. Submicron patterns with a high aspect ratio can easily be obtained with this bilayer resist process.

INTRODUCTION

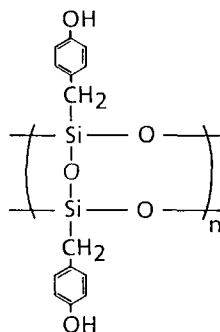
In our previous article we mentioned that development of alkali-developable organosilicon positive photoresists for a bilayer resist system has been important in solving many problems associated with nonplanar device topography and surface reflectivity in semiconductor lithography.¹⁻³

The reported resists belong to a category of conventional dissolution-inhibition resists, which are composed of alkali-soluble polymers, such as novolac resin and photoactive compounds (dissolution inhibitors) such as naphthoquinone diazide, and are different in how they introduce silicon atoms into the resist. The first type of resist contains organosilicon substituents in the polymer side chain.⁴⁻⁸ The second type of resist includes silicon atoms in the polymer main chain.⁹⁻¹² The third type of resist adds organosilicon compounds into the conventional re-

sists.¹³ We reported, just prior to this article, syntheses and characterization of three alkali-soluble organosilicon polymers (silsesquioxane, siloxane, and silylmethylene polymers with phenolic hydroxy groups) and selected poly(*p*-hydroxybenzylsilsesquioxane) (**1**), illustrated in Scheme 1, as the best matrix resin of organosilicon resist, taking into consideration O₂RIE resistance and the thermal properties. In this article, we present characteristics of novel alkali-developable organosilicon positive photoresist using **1** as the matrix resin, which belongs to the second type.

Another serious problem encountered in the bilayer resist process is the difficulty in the stripping of organosilicon resists. It has been pointed out that in the case of the trilayer resist system, the top conventional resist can be eliminated by the usual wet procedure or dry etching, but the organosilicon resist cannot be stripped by the same procedures. No report has described such a problem in detail. In this article, we also present a study on the stripping method as well as the bilayer resist process using the above-mentioned resist.

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Scheme 1 Molecular structure of poly(*p*-hydroxybenzylsilsequioxane) (**1**).

EXPERIMENTAL

Materials

Poly(*p*-hydroxybenzylsilsequioxane) (**1**) was used as the matrix resin. The preparative method and the properties were described in the previous article. Esters (**2**) (Toyo Gosei Kogyo), prepared from 1,2-naphthoquinone diazide-5-sulfonylchloride and 2,3,4-trihydroxybenzophenone, were examined as the photoactive compounds. Scheme 2 shows the structure of its main component: triester. 1-Acetoxy-2-ethoxythane was adopted as the solvent. Tetramethylammonium hydroxide, trimethyl-2-hydroxyethylammonium hydroxide, methyl-tris (2-hydroxyethyl) ammonium hydroxide, and tetrakis (2-hydroxyethyl) ammonium hydroxide were investigated as organic alkalis of the developer. S-502 (Tokyo Ohka Kogyo), S-10 (Tokyo Ohka Kogyo), fluoric acid, a mixture of dimethylsulfoxide and piperidine, and sulfuric acid were examined as the stripper. OFPR-800 (Tokyo Ohka Kogyo) was used as a reference resist. PIQ (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 1 μm -thick layer, were spin-coated on silicon wafers that had been previously coated with a 2 μm -thick PIQ, and were prebaked for 30 min at 85–90°C. Ultraviolet exposure was carried out using a contact aligner (Cobilt AF-2800H), equipped with a 250 W high pressure mercury arc lamp or *g*-line stepper (NA = 0.35) (Hitachi). The development was carried out by dipping in aqueous, organic alkalis for 1 min at 25°C. The UV intensity was measured at 365 nm using an irradiance tester (Ushio Electric UIT-100). The spectral sensitivities

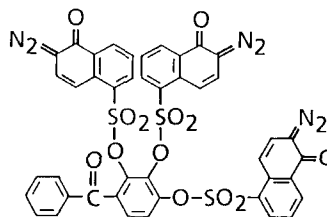
were measured using a grating monochrometer (Narumi RM23-I-64), equipped with a logarithmic slit and 1 kW Xenon arc lamp. O₂RIE was carried out using a parallel plate reactor with the conditions as follows: RF, 0.64 mW/cm²; O₂ pressure, 20 mtorr; Self-bias, –120––140 V. The resist stripping was carried out by dipping in hydrogen fluoride/ammonium fluoride (1:20 w/w) for 5 s, followed by immersion in S-10 for 5 min at 60°C.

RESULTS AND DISCUSSION

Resist Composition

Prior to this study, we synthesized three alkali-soluble organosilicon polymers (silsequioxane, siloxane, and silmethylene polymers with phenolic hydroxy groups) and selected poly(*p*-hydroxybenzylsilsequioxane) (**1**) as the best matrix resin of organosilicon resist. Polymer **1** is alkali-soluble and has excellent O₂RIE resistance: the O₂RIE rate is 2.3 nm/min while that of PIQ is 122 nm/min and thermal properties: $T_g = 107^\circ\text{C}$, $T_d = 373^\circ\text{C}$.

As the photoactive compounds, esters (**2**) prepared from 1,2-naphthoquinone diazide-5-sulfonylchloride and 2,3,4-trihydroxybenzophenone were investigated. Practically, **2** is used in a mixture form and the triester content in the mixture affects the exposure characteristics. Figure 1 shows the effect of the triester content in **2** on sensitivity and remaining film thickness of 1 μm -thick resist (**1** : **2** = 80 : 20 w/w) formed on a 2 μm -thick PIQ. The development was carried out with 0.45 wt % aqueous tetramethylammonium hydroxide for 3 min at 23°C. The remaining film thickness increases gradually according to increases in triester content; the sensitivities also increase, but are saturated above 75 mol %. Here it should be noted that the pot life of **2** gets shorter as the triester content in **2** increases. This is due to precipitation of insoluble impurities. Generally the precipitation is fairly restrained by incorporation of matrix resins, such as novolac. However, in the case of **1**, the restraint was weaker



Scheme 2 Molecular structure of the main component in the photoactive compound (**2**).

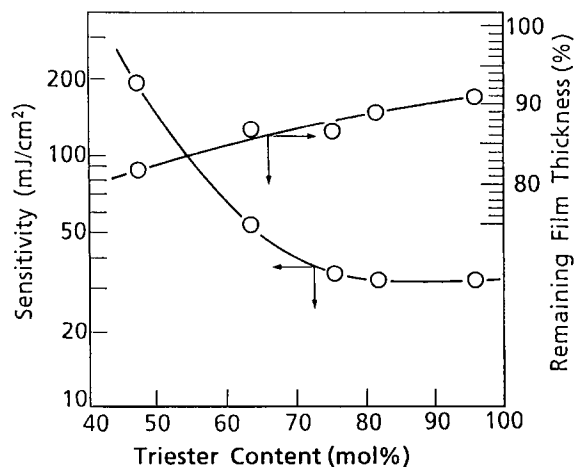


Figure 1 Effects of the triester content in **2** on the sensitivity and the remaining film thickness of 1 μm -thick resist (1:2 = 80:20 w/w).

compared to novolac. So we adopted **2**, of which the triester content was from 70 to 80 mol % as the photoactive compound. Furthermore, a combination of **1** and esters prepared from 2,3,4,4'-tetrahydroxybenzophenone was also available.

Next we optimized the ratio of **1** to **2**. Figure 2 demonstrates the effect of **2** content in the resist on the sensitivity of 1 μm -thick resist formed on a 2 μm -thick PIQ. The experiment was carried out with aqueous tetramethylammonium hydroxide having, each optimized concentration such that 90% of the film thickness still remained after 1 min at 25°C. The sensitivity increases according to increases in **2** content and is saturated above 30 wt %. On the

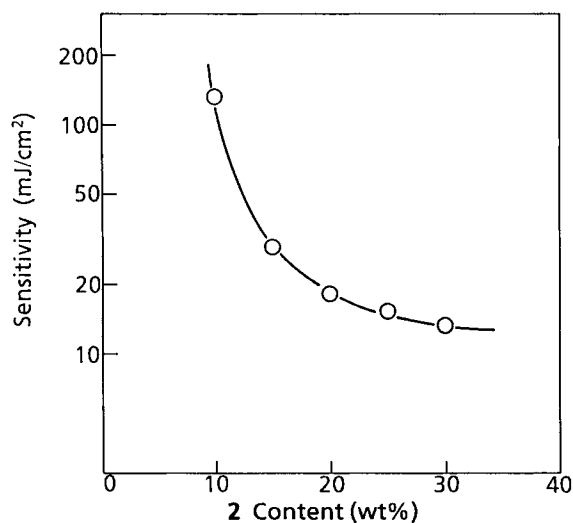


Figure 2 Effects of **2** content in the resist on the sensitivity of 1 μm -thick resist.

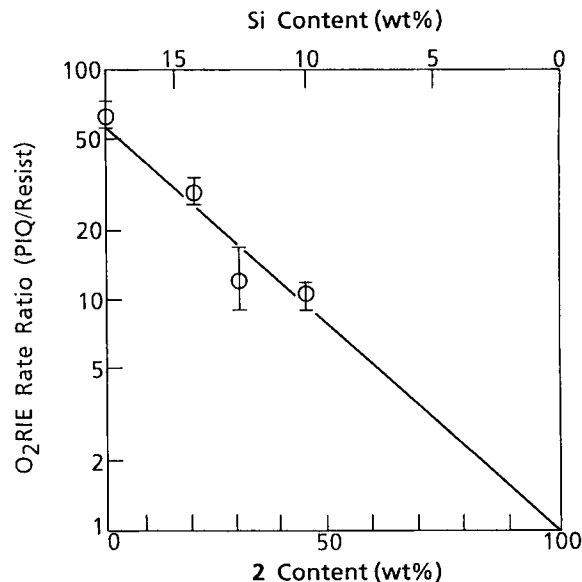


Figure 3 Effect of **2** content in the resist on the O₂RIE resistance.

other hand, the O₂RIE resistance decreases according to increases in **2** content, as shown in Figure 3. Thus, we fixed the **2** content in the resist at 20 wt % for the present.

At this point, we designated this resist OSPR-1334 (OSPR: *Organosilicon Positive Resist*). The matrix resin is **1** and the photoactive compound is **2**, of which the triester content is from 70 to 80 wt %. The solvent is 1-acetoxy-2-ethoxyethane. The ratio of **1** to **2** is 80 : 20 w/w.

Developer

Usually, aqueous tetramethylammonium hydroxide is used as a developer for novolac-based resists. However, we found that aqueous tetrakis (2-hydroxyethyl) ammonium hydroxide is a suitable developer for OSPR-1334. Figure 4 illustrates the effect of organic alkali in the developer on the sensitivity of 1 μm -thick OSPR-1334 formed on a 2 μm -thick PIQ. The development was carried out with each developer having an optimized concentration (90% film thickness remaining after 1 min at 25°C). The successive exchange of the methyl group in tetramethylammonium hydroxide for the 2-hydroxyethyl group brings about the enhancement of the sensitivity of OSPR-1334 and a decrease in the alkali-normality of the developer. The reduction of the alkali-normality suggests an increasing solubility of **1**. This phenomenon is opposite in the case of novolac-based resists. The photoactive compounds of novolac-based resists are also naphtho-

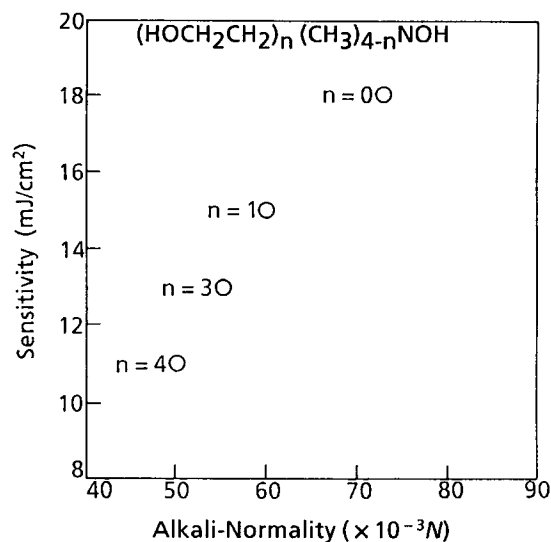


Figure 4 Effect of organic alkalis in the developer on the sensitivity of 1 μm -thick OSPR-1334.

quinone diazide, and the difference between **1** and novolac resin exists only in the polymer skeletons. Therefore, the prime cause of the increasing solubility can be considered as the interaction between oxygen of the polymer main chain of **1** and hydroxyethyl group of the developer as shown in Figure 5. This results in the relative enhancement of the solubility difference between exposed areas and unexposed areas.

Characteristics of OSPR-1334

The characteristics of 1 μm -thick OSPR-1334 formed on a 2 μm -thick PIQ were compared with those of a reference resist: OFPR-800. Figure 6 shows the comparison of spectral sensitivities. Both resists have almost the same sensitive region which includes the *i*-line and *g*-line. Figure 7 shows the

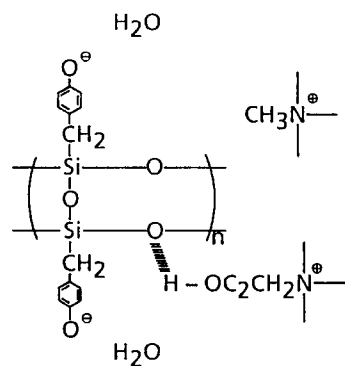


Figure 5 Interaction between **1** and organic alkalis.

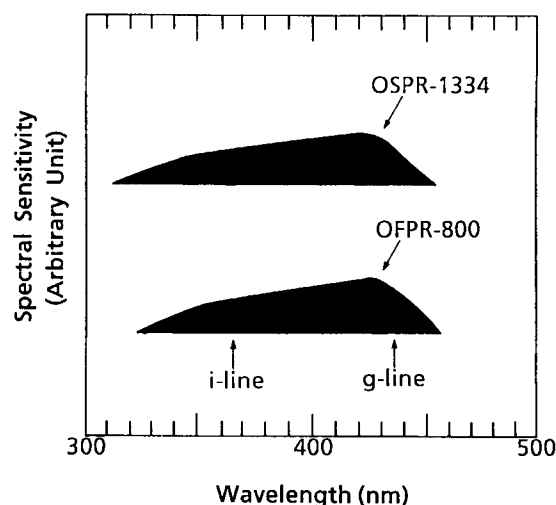


Figure 6 Spectral sensitivity comparison of OSPR-1334 and OFPR-800.

comparison of exposure characteristics. The sensitivity, the γ -value, and the remaining resist thickness are almost the same in both resists. The sensitivity is 11 mJ/cm^2 , measured at 365 nm, the γ -value is 1.8, the remaining resist thickness is above 90% based on this development condition: 0.050 *N* aqueous tetrakis(2-hydroxyethyl) ammonium hydroxide for 1 min at 25°C. Figure 8 shows SEM photographs of OSPR-1334 and OFPR-800 patterns. The 0.75 μm lines and 0.75 μm spaces can be resolved with a contact aligner, and the resolution in both resists can be regarded as the same, compared with

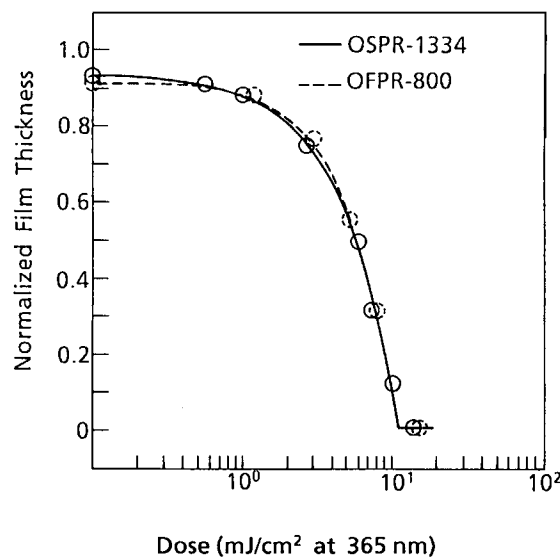
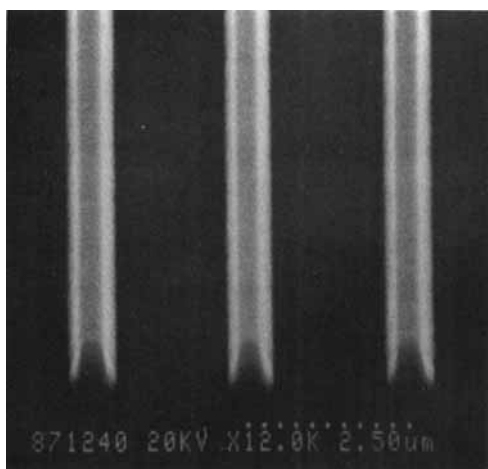
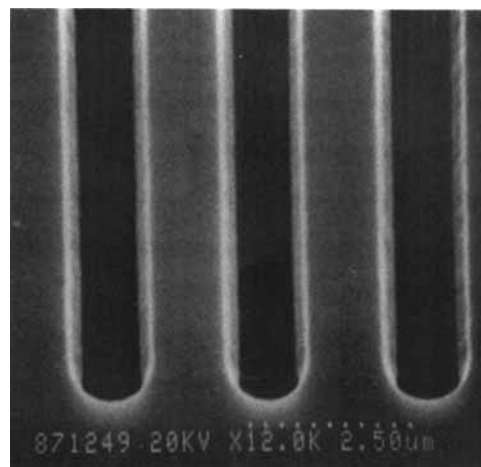


Figure 7 Exposure characteristic comparison of OSPR-1334 and OFPR-800.

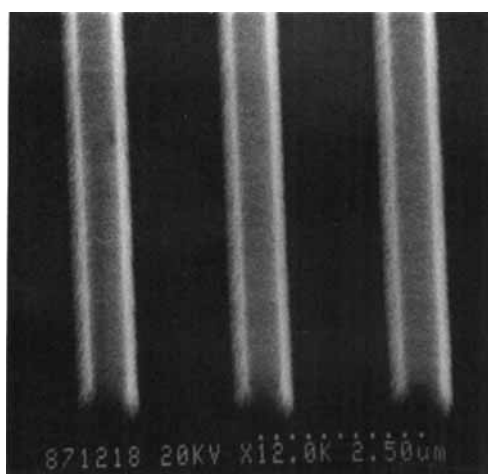


(a)

OSPR-1334

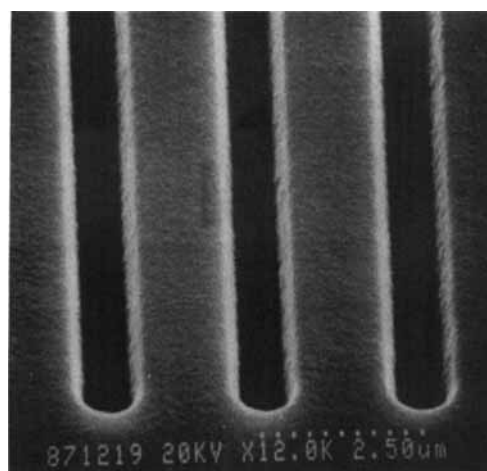


(b)



(c)

OFPR-800



(d)

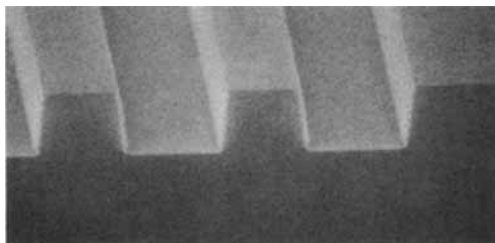
Figure 8 SEM photographs of OSPR-1334 and OFPR-800 patterns on PIQ printed by a contact aligner. (a,c) 0.75 μm lines, (b,d) 0.75 μm spaces.

the profiles of both resist patterns. Figure 9 shows SEM photographs of line and space patterns of OSPR-1334 on a silicon wafer using a *g*-line stepper (NA = 0.35) and Figure 10 shows the relation between the mask width and pattern width in OSPR-1334. The linearity is kept up to 0.8 μm lines and spaces. Figure 11 shows the O_2RIE resistance of OSPR-1334. The etching rate of OSPR-1334 is 3.6

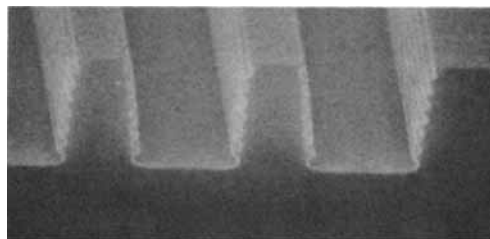
nm/min, while that of PIQ and OFPR-800 is 100 nm/min; the etching rate ratio is 28. OSPR-1334 has excellent O_2RIE resistance.

Bilayer Resist Process Using OSPR-1334

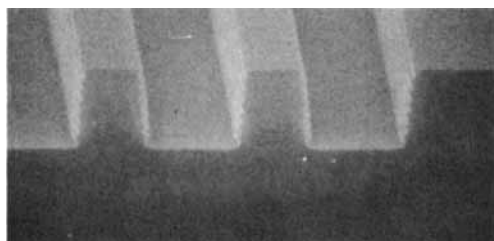
Actual fine patterns of OSPR-1334 could be transferred to the bottom layer (PIQ) by O_2RIE . Figure



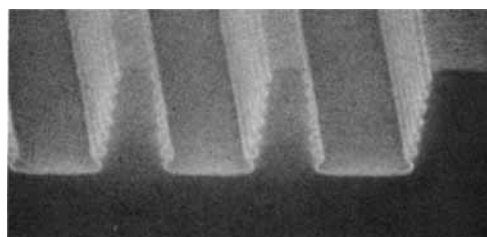
1.40 μm L & S



1.00 μm L & S



0.80 μm L & S



0.70 μm L & S

Figure 9 SEM photographs of OSPR-1334 patterns on a Si wafer printed by a *g*-line stepper (NA = 0.35).

12 shows SEM photographs of the resist patterns before and after O₂RIE. Fine bilayer resist patterns can be obtained easily in this manner.

A surface of OSPR-1334 after O₂RIE had been

expected to consist of pure silicon oxide. Therefore, we first tried to strip OSPR-1334 using fluoric acid for the surface layer and a conventional stripper, S-502 (Tokyo Ohka), for the unchanged layer. How-

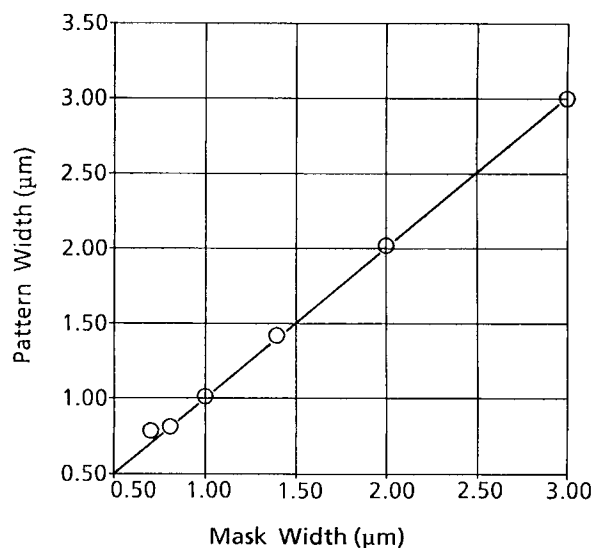


Figure 10 Linearity between the mask width and the pattern width in OSPR-1334.

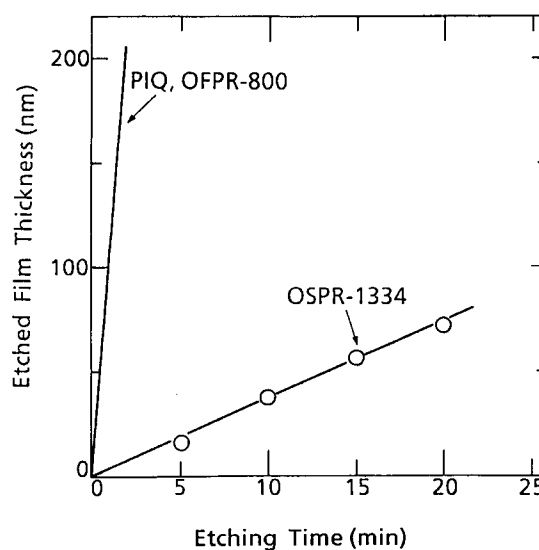
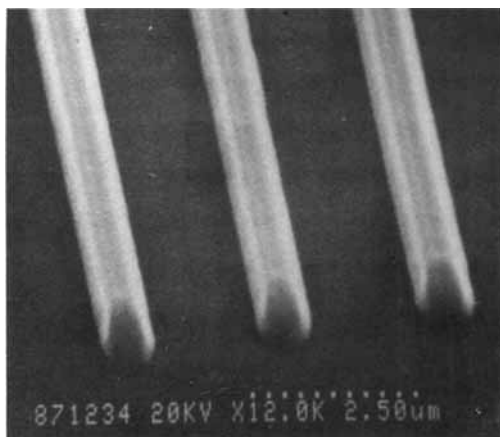
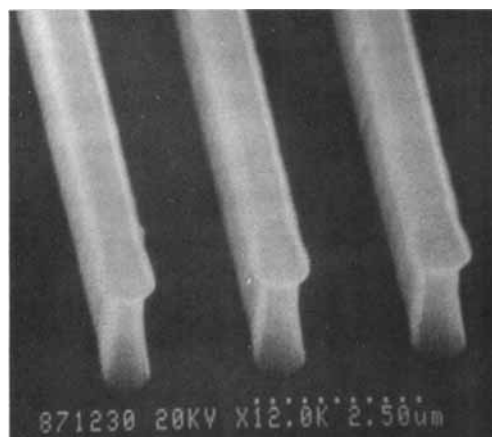


Figure 11 O₂RIE resistance of OSPR-1334, OFPR-800, and PIQ.



before O₂RIE



after O₂RIE

Figure 12 SEM photographs of OSPR-1334 patterns before and after O₂RIE.

ever, the surface layer was not soluble in fluoric acid and it was attached to PIQ, leaving the shape as shown in Figure 13. XPS analysis in Figure 14 indicates that the surface layer contains not only silicon-oxygen bonds, but also silicon-carbon bonds, which have a strong bonding energy. We then looked for solvents that could cleave the silicon-carbon bond and dissolve perfectly the surface layer and the unchanged layer, but we found only sulfuric acid worked. Sulfuric acid is, of course, not suitable for practical use. Thus, we concluded that it was difficult to dissolve the surface layer, and looked for solvents that could dissolve the unchanged layer; we did not make the surface layer attach to PIQ. Such solvents

were organic amines, for instance, a mixture of dimethylsulfoxide and piperidine, and a conventional stripper S-10 (Tokyo Ohka). The developer was also useful if a postexposure was carried out before O₂RIE. Floating surface layers in the solvent could be eliminated by spinning out with centrifugal force or filtration.

Furthermore, a side wall was found to be attached to PIQ. Figure 15 shows a SEM photograph of the side wall, which fell on the silicon wafer from a PIQ wall while the treatment with sulfuric acid was carried out. This side wall might be composed of pure sputtered silicon oxide, originating from the surface layer, because it was not soluble in sulfuric acid but

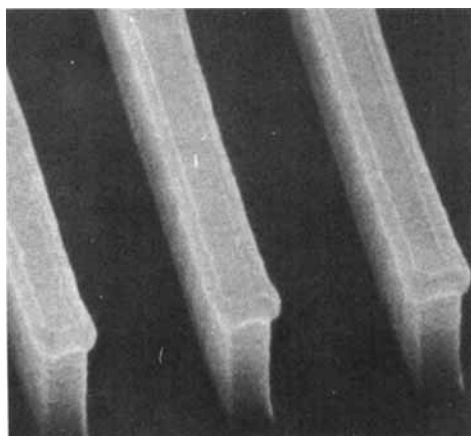


Figure 13 SEM photograph of PIQ patterns after stripping of OSPR-1334 with S-502.

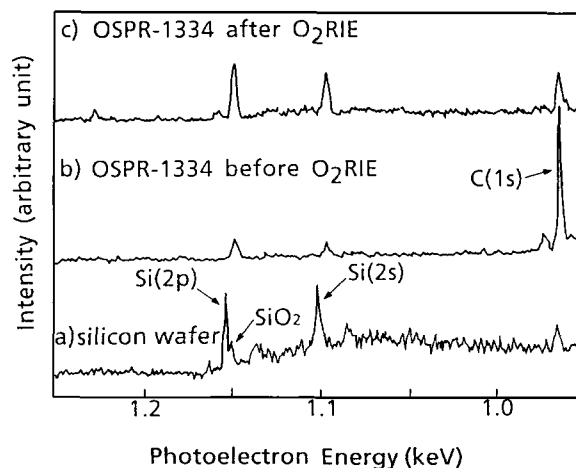


Figure 14 XPS analysis of the surface of OSPR-1334 before and after O₂RIE.

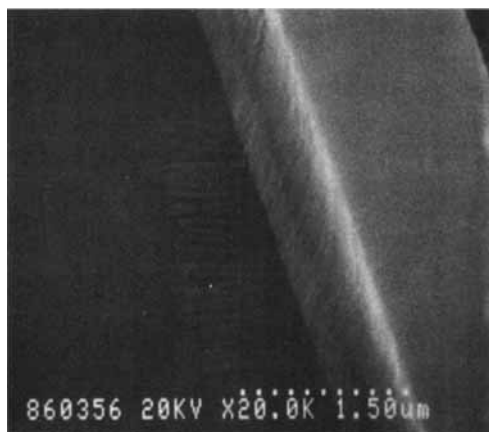


Figure 15 SEM photograph of a side wall, which fell on a silicon wafer from a PIQ wall.

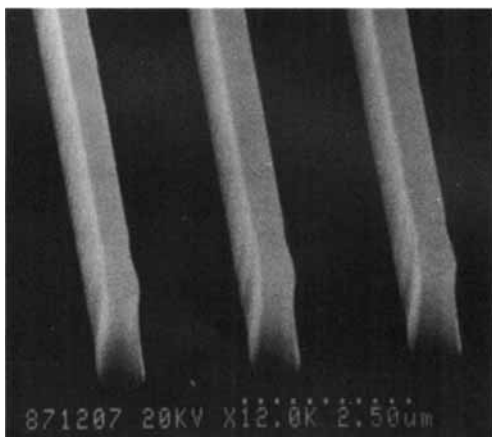


Figure 16 SEM photograph of PIQ patterns after stripping of OSPR-1334 by treating with fluororic acid and S-10.

soluble in dilute fluororic acid. Therefore, we added a treatment with dilute fluororic acid before the above-mentioned stripping process.

Figure 16 shows a SEM photograph of PIQ patterns after dipping in hydrogen fluoride/ammonium fluoride (1 : 20 w/w) for 5 s, followed by immersion in S-10 for 5 min at 60°C.

CONCLUSIONS

A new alkali-developable organosilicon positive photoresist (OSPR-1334) was developed for the bi-

layer resist system. OSPR-1334 prepared from poly(*p*-hydroxybenzylsilsequioxane) and naphthoquinone diazide has excellent O₂RIE resistance and has almost the same properties as those of conventional novolac-based resists, with respect to sensitivity, spectral sensitivity, and resolution. Submicron patterns can be obtained easily using OSPR-1334 as the top layer in the bilayer resist system. OSPR-1334 after O₂RIE can be eliminated by dissolving the unchanged layer, followed by spinning out or filtrating the changed surface layer.

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