Organosilicon Deep UV Positive Resist Consisting of Poly(p-disilanylenephenylene)

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Synopsis

A new class of positive deep ultraviolet (UV) resists consisting of poly(p-disilanylenephenylene)s was developed, in which a disilanylene unit and a phenylene unit are connected alternatively in the polymer main chain. These resists had very high etching resistance against oxygen plasma. The lithographic applications of a double-layer resist system in which the poly(p-disilanylenephenylene) film was used as the top imaging layer were examined. As a result, very high resolution and high contrast were attained. The double-layer resist technique using organosilicon deep UV positive resist appears very promising for lithographic applications.

INTRODUCTION

The very large-scale integrated (VLSI) technology has created increasing demands on photolithography for new materials and processes to offer submicron resolution with accurate line-width control. But in nonplanar wafers, there are several obstacles in achieving this resolution. In single-layer resist film, for example, high resolution becomes difficult due to diffraction and scattering in the resist film, halation of ultraviolet (UV) light over the wafer topography, and difference in developing time due to varying thicknesses of the resist film. Recently, the multilayer resist system has been studied with a view toward solving these problems,[1-3] and the triple-layer resist method is expected to be a promising lithographic process to achieve high resolution. However, the present method must be shortened and simplified.

Organosilicon resists have been reported to show resistance against oxygen plasma, and to be able to act as the top imaging layer in the double-layer method, which is the simplest multilayer resist system. The reported typical organosilicon polymers for lithographic applications are the siloxane polymers having vinyl groups,[4] or chloromethyl groups[5] and polystyrene having trimethylsilyl groups.[6] All of them are negative electron-beam resists or deep UV resists. Polysilanes have also been seen to serve as excellent O_2-reactive ion-etching barriers for double-layer resist applications.[7]

As part of an investigation dealing with photochemistry of polymeric organosilicon compounds containing disilanyl units,[8] we have prepared p-disilanylenephenylene polymers and examined some features of their photochem-

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ical behavior in the hope of obtaining a new class of positive deep UV resists, which can act as the top imaging layer in double-layer resist applications.

This paper discusses the lithographic characteristics of the deep UV-sensitive poly(*p*-disilanylenephenylene) film and the double-layer system which uses it as the top imaging layer.

EXPERIMENTAL

Synthesis

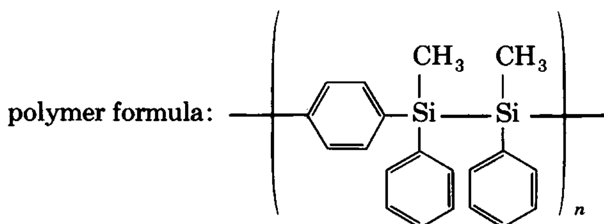
The synthesis of poly(*p*-1,2-dimethyldiphenyldisilanylenephenylene) is described in the following. Other polymers of several (*p*-disilanylene)phenylenes were synthesized in the same way.

Synthesis of poly(*p*-1,2-dimethyldiphenyldisilanylenephenylene). A 500 mL, three-necked, round-bottomed flask was fitted with a reflux condenser, a motor-driven stirrer, and a pressure-equalizing dropping funnel. This apparatus was thoroughly dried and purged with dry nitrogen. All subsequent reaction operations were carried out under a nitrogen atmosphere.

Methylphenyldiethoxysilane, 21.0 g, of magnesium, 2.43 g, and 100 mL of tetrahydrofuran solution containing 11.8 g of *p*-dibromobenzene was added dropwise from the dropping funnel for about 3 h while the mixture was stirred. After the dropwise addition, the resulting solution was filtered and then the solvent was removed by distillation. The residues were then subjected to distillation under reduced pressure, whereby 15 g of *p-bis*(methylphenylethoxysilyl)benzene (boiling point: 213–215°C/3 mmHg) was obtained (yield: 78%).

Nuclear magnetic resonance (NMR) spectrum (CCl_4) δ (ppm): 0.76 (3H, s, CH_3—Si), 1.36 (3H, t, CH_3—C), 3.94 (2H, q, CH_2—OSi), and 7.4–7.8 (7H, m, ring protons): 9.2 g of the thus obtained *p-bis*(methylphenylethoxysilyl) benzene and 25 g of acetyl chloride were refluxed for about 5 h, whereby 8.2 g of *p-bis*(chloromethylphenylsilyl)benzene (boiling point: 229–232°C/3 mmHg) was obtained (yield: 94%).

NMR spectrum (CCl_4) δ (ppm): 1.00 (3H, s, CH_3—Si), and 7.5–7.8 (7H, m, ring protons): Next, a 300 mL, three-necked, round-bottomed flask was fitted with a reflux condenser, a motor-driven stirrer, and a pressure-equalizing dropping funnel. A 100 mL toluene dispersion solution containing 5 g sodium was placed in the flask and 100 mL of a benzene solution containing 15 g of *p-bis*(chloromethylphenylsilyl)benzene was slowly added through the funnel. During this time the mixture was vigorously stirred and heated at 70–80°C for 20 h. After heating, the resulting product was reprecipitated by a benzene–ethanol (1 : 1 by vol) solution, whereby white powder of polymer having the following composition was obtained in a yield of about 65%.



The properties and analytical results of the thus obtained polymer are given below.

Melting point:	155–163°C
Weight average molecular weight:	34,000
NMR spectrum (C_6D_6) δ (ppm):	0.64 (3H, s, Me—Si), 7.26 and 7.36 (7H, ring protons)
IR spectrum:	3080, 3060, 2980, 1435, 1385, 1260, 1130, 1110, 1000 cm^{-1}
UV spectrum:	λ_{max} 270 nm

Resist Processing

Resist Preparation. Resist solutions were prepared by dissolving the poly(*p*-disilanylenephenylene) in toluene by 5–10 weight percent. The solutions were then filtered through a 0.5 μm teflon filter.

Spin Coating. Resist films were spin-coated on silicon wafers at 2000 rpm using a conventional spinner.

Baking. The resist films were prebaked in a conventional oven at 120°C for 30 min.

Exposure. Deep UV exposure was carried out using a Canon contact aligner PLA-521FA in air. Some samples were exposed in an inert atmosphere, such as in N_2 flow conditions.

Developing and Rinsing. The developer used in this study was a mixture of toluene–isopropanol (1 : 5 by vol.). Developing was carried out by immersion in a bath at 25°C for 15 s without agitations. Isopropanol was used as the rinser and rinsing was carried out by immersion in a bath at 25°C for 15 seconds.

Plasma Etching

O_2 plasma-etching resistance of several polymer films was evaluated using an O_2-reactive ion-etching apparatus. The resist film thickness removed during O_2-reactive ion etching was measured by using a Talystep film thickness gauge.

Image Evaluation

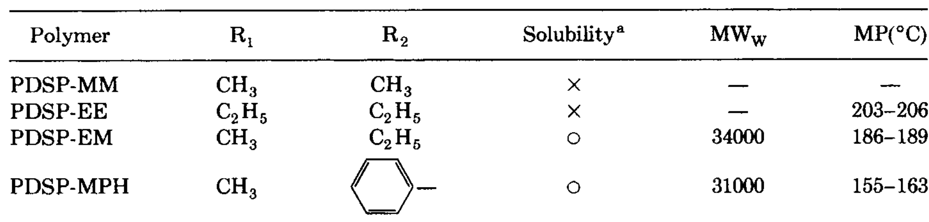
The quality of images in the resist patterns was evaluated with a Hitachi electron microscope.

RESULTS AND DISCUSSION

Basic Properties of Poly(*p*-disilanylenephenylene)s

Several poly(*p*-disilanylenephenylene)s (PDSP) with different organic substituents (i.e., methyl, ethyl, and phenyl groups) were synthesized in order to vary the polymer properties. The basic properties of PDSP are shown in Table I. When PDSP had the same organic substituents ($R_1 = R_2$), the polymers (PDSP-MM and PDSP-EE) were barely soluble in organic solvents and unable to be used as photoresists. On the other hand, when R_1 and R_2 were different, the polymers were soluble in common organic solvents (i.e., toluene). This solubility was attributed to the loss of molecular symmetry by

TABLE I
Properties of PDSP

Polymer	R_1	R_2	Solubility[a]	MW_W	MP(°C)
PDSP-MM	CH_3	CH_3	×	—	—
PDSP-EE	C_2H_5	C_2H_5	×	—	203–206
PDSP-EM	CH_3	C_2H_5	○	34000	186–189
PDSP-MPH	CH_3		○	31000	155–163

[a]Solvent: Toluene.

the introduction of differing bulky substituents. PDSP-EM in which R_1 and R_2 were methyl and ethyl groups, respectively, and PDSP-MPH in which R_1 and R_2 were methyl and phenyl groups, respectively, were used in order to examine photosensitivity and other properties. The average molecular weights of these polymers were about 30,000, and their melting points were very high, about 160–190°C.

The UV spectra of PDSP were measured. PDSP-EM and PDSP-MPH had λ_{max} at 262 and 270 nm, respectively, which were at wavelengths 30 to 40 nm longer than the absorbances for pentamethyldisilane (λ_{max}: 236 nm) and 1,2-diphenyltetramethyldisilane (λ_{max}: 236 nm) which are typical disilane compounds.

Heat Resistance of PDSP

The thermal gravimetric analyses of PDSP-MPH were measured in air and in N_2 with the results shown in Figure 1. As shown here, the weight loss

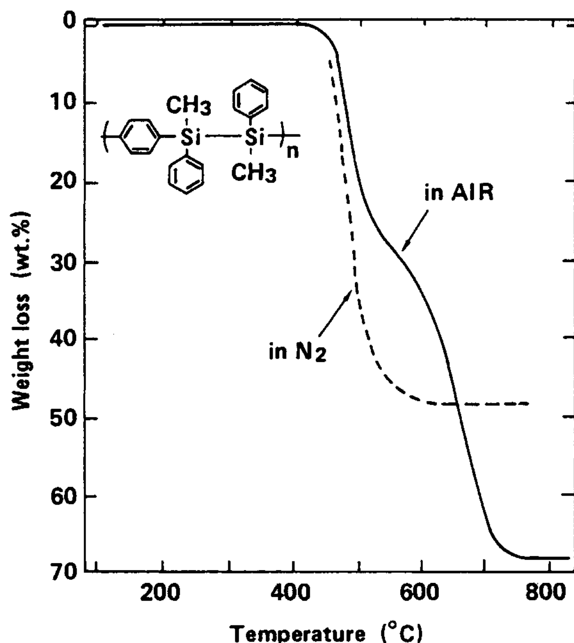


Fig. 1. TGA curve of PDSP-MPH.

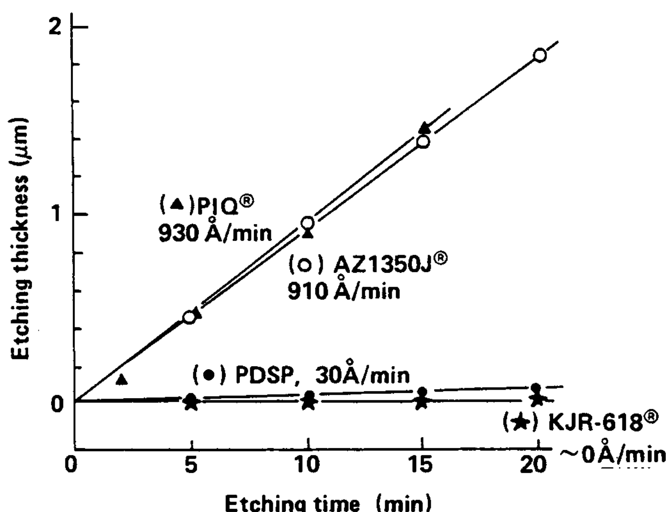


Fig. 2. Etching rate of organic polymers by O_2 RIE.

occurred at about 400°C; thus PDSP had excellent heat resistance compared with conventional photoresists.

O_2-Reactive Ion-Etching Resistance of PDSP

The O_2-reactive ion-etching rates of PDSP and conventional organic polymers were measured under the following experimental conditions: RF power, 0.64 W · cm^{-2}(7 MHz); O_2 pressure, 3 mtorr; and cathode bias voltage, −120 to −100 V. Figure 2 shows the change in etching thickness vs. etching time. Interestingly, PDSP demonstrated a very high etching resistance against oxygen plasma, compared with ordinary organic polymers. For the conditions cited, PDSP had an oxygen plasma-etching resistance about 30 times that of polyimide, PIQ, or the phenolnovolac resin, AZ-1350J. Its etching rate was 30 A/min. Under the same conditions, siloxane polymer, KJR-618 showed hardly any change. Thus, the siloxane structure provided good resistance to oxygen plasma.

Photosensitivity of PDSP

As mentioned above, PDSP had a strong absorption in the UV region and it acted as a positive photoresist, both expected reactions. The spectral sensitivity of PDSP-MPH was measured, and is shown in Figure 3. It was photosensitive in the deep UV region of 250–300 nm. The exposure characteristics of PDSP-EM are shown in Figure 4, compared with conventional photoresists. As shown here, PDSP-EM acted as a positive photoresist, but after development a residue was observed in the exposed region. It appeared that a recombination reaction occurred in parallel with the degradation reaction. Then, the addition of radical trap agents was studied to prevent residue formation and enhance photosensitivity. The addition of 2,6-di-*t*-butyl-*p*-cresol provided suitable sensitivity for this. On the other hand, the exposure characteristics of PDSP-MPH were also measured and are shown in Figure 5. After development, no residue was observed; PDSP-MPH acted as a good positive working photoresist. The sensitivity depended on the thickness of

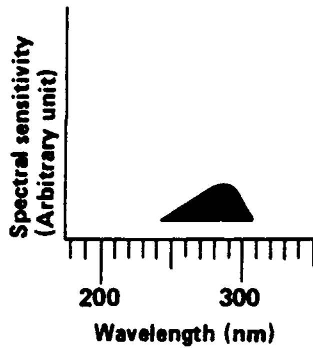


Fig. 3. Spectral sensitivity of PDSP-MPH.

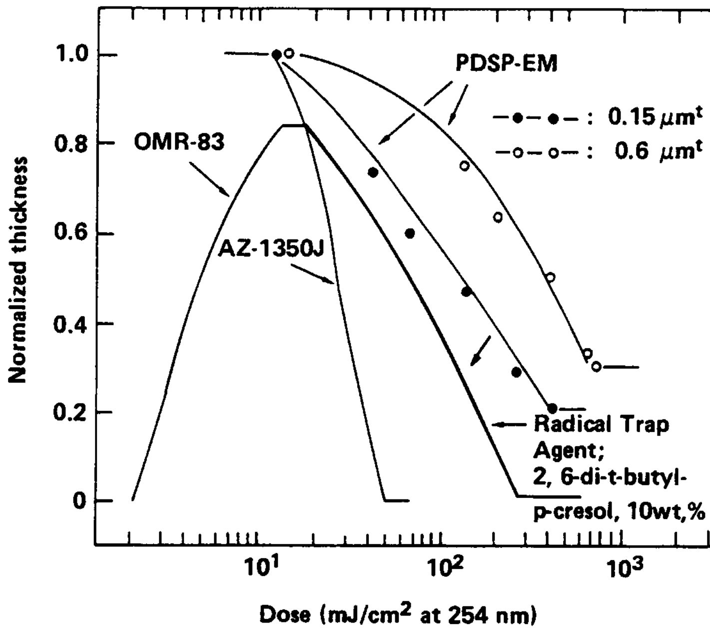


Fig. 4. Exposure characteristics for photoresist on UV irradiation.

resist film, and was improved by the addition of the radical trap agent, just as in the case of PDSP-EM. The sensitivity was 220 mJ/cm^2 at 0.2 μm thickness.

Photodegradation Mechanism of PDSP

As mentioned above, it was ascertained that PDSP acted as a positive photoresist by deep UV exposure in air. Also, the polymer image pattern was obtained by exposure under an inert atmosphere, such as in N_2 flow conditions. The mechanism of its photodegradation in air was investigated.

The UV spectra of PDSP-MPH are shown in Figure 6. The absorption attributed to the conjugation of the Si—Si bond and phenylene group was greatly decreased after UV irradiation. This indicated that Si—Si bonds in the polymer main chains were photochemically scissored.

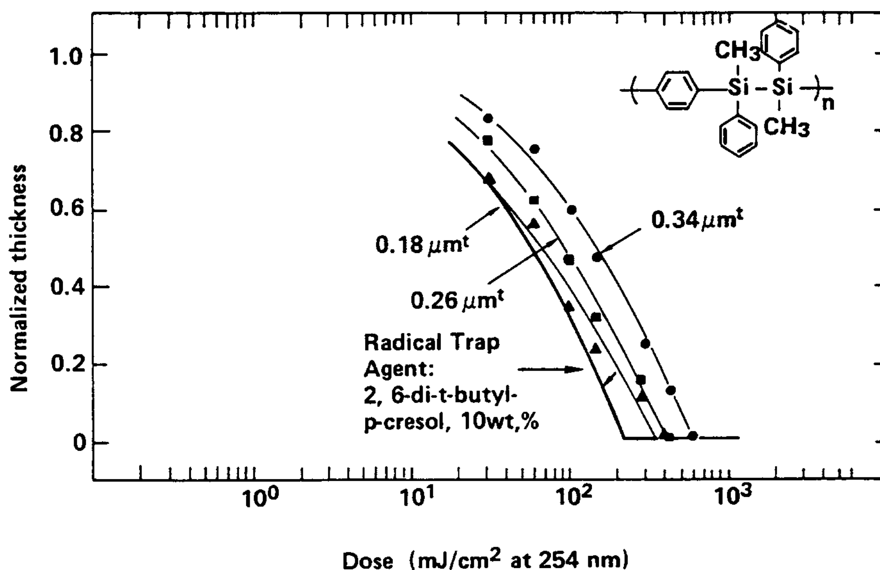


Fig. 5. Exposure characteristics for PDSP-MPH on UV irradiation.

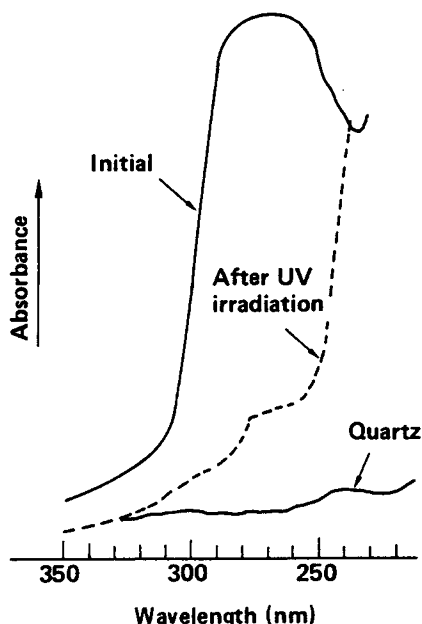


Fig. 6. UV spectra of PDSP-MPH.

Next, changes in the molecular weight were examined. As shown in Figure 7, molecular weight decreased with UV irradiation. Clearly, photodegradation products of lower molecular weight were produced by scission of the polymer main chain.

The infrared spectra of PDSP-MPH before and after UV irradiation are shown in Figure 8. The bottom spectrum represents the differential one obtained subtracting the initial one from that after UV irradiation. New

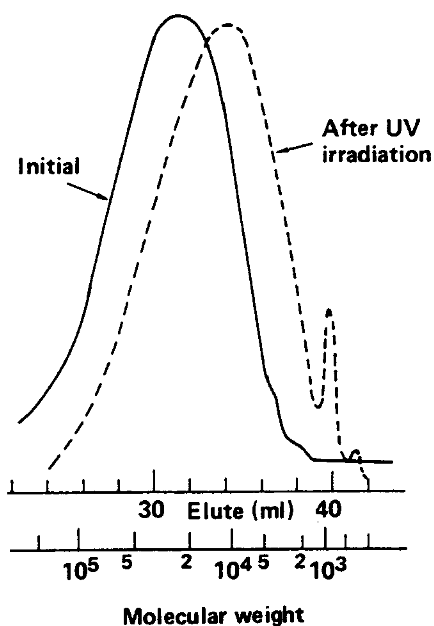


Fig. 7. Liquid chromatograph of PDSP-MPH.

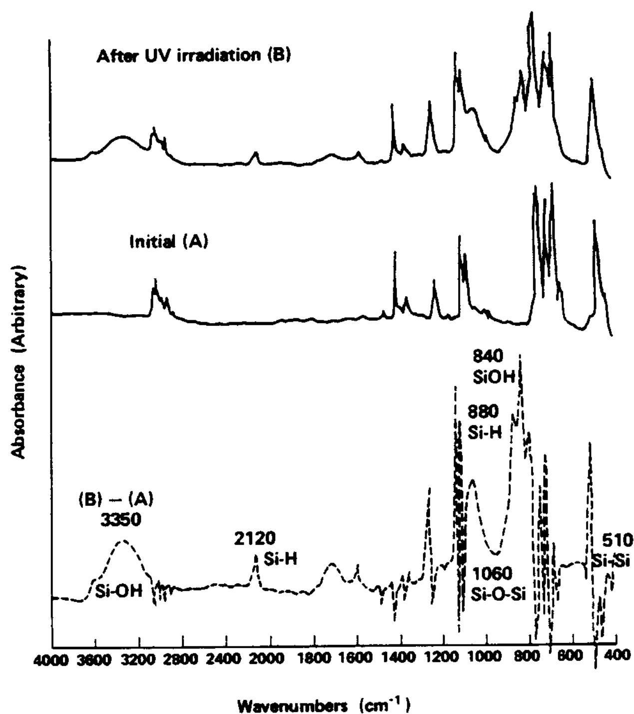
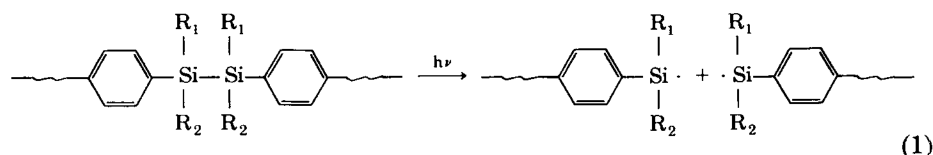


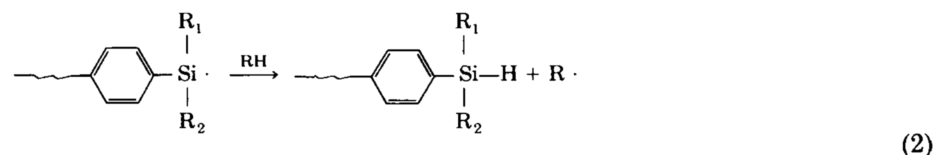
Fig. 8. Infrared spectra of PDSP-MPH.

characteristic bands were observed at 3350 cm^{-1} (Si—OH bond), 2120 cm^{-1} (Si—H bond), and 1060 cm^{-1} (Si—O—Si bond). And the characteristic band at 510 cm^{-1} (Si—Si bond) became smaller. It was obvious that Si—Si bonds were scissored, but judging from the formation of Si—O—Si bonds, it was proposed that silyl radicals recombined with oxygen molecules.

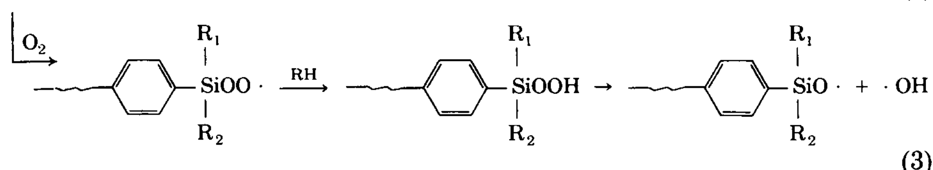
These results may be explained by the following photodegradation scheme (1)–(5). The radical scission of Si—Si bonds in the polymer main chain is photochemically induced [Eq. (1)] and then produced silyl radical reacts a hydrogen donor [Eq. (2)] or oxygen molecules to produce photodegradation products which have Si—H, Si—O—Si, or Si—OH bonds.



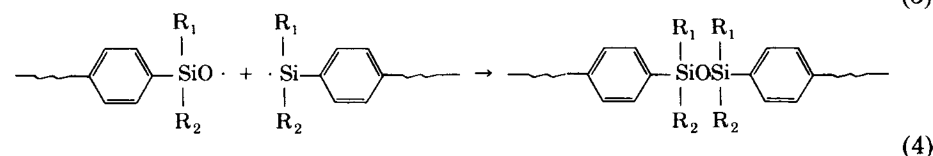
(1)



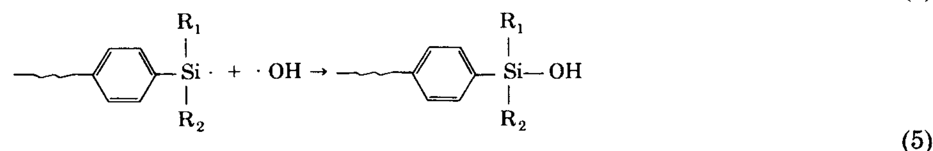
(2)



(3)



(4)



(5)

Double-Layer Resist System

The double-layer resist system using PDSP (0.2 μm thick) as a top imaging layer was studied. The experimental conditions are described below.

The polyimide, PIQ (2.0 μm thick) was used as an underlayer. The UV exposure was carried out using the Canon contact aligner, PLA-521FA, and the exposure time was 5 to 6 s, where UV intensity was 72 mW/cm^2 at 254 nm. After UV irradiation, a positive resist pattern was obtained on the development using toluene–isopropanol (1 : 5 by vol.) for 15 s, and rinsing in isopropanol for 15 s. The O_2-reactive ion etching was carried out under the condition of 0.64 W/cm^2 (7 MHz, of RF power and 3 mtorr of O_2 pressure).

Fig. 9. Double-layer resist pattern (deep UV exposure-O_2 RIE).

The scanning electron micrographs (SEM) of a double-layer resist pattern are shown in Figure 9. Submicron level line patterns could be obtained easily, where the minimum line width was 0.5 μm and the aspect ratio was above 3.0.

CONCLUSION

A new class of positive deep UV resists consisting of poly(*p*-disilanylenephenylene) (PDSP) was developed, and investigated in regard to application in a double-layer resist system. Some resist characteristics were elucidated as follows:

1. The radical scission of Si—Si bonds in the polymer chains was induced photochemically.
2. Their photosensitivity was enhanced by the addition of radical trap agents.
3. The PDSP resists had high resistance against O_2 plasma compared to ordinary organic polymers.
4. Using PDSP as the top imaging layer in the double-layer resist system, submicron-level line patterns could be obtained easily, where the minimum line width was 0.5 μm and the aspect ratio was above 3.0.

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