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(56) Documents cited

None

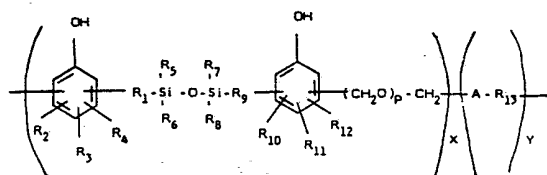
(58) Field of search

C3T

Selected US specifications from IPC sub-class C08G

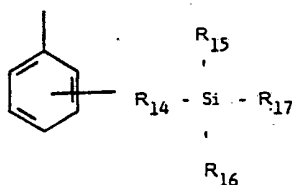
(54) **Photoresist materials**

(57) A photoresist material comprising a polymer having recurring units of the formula:



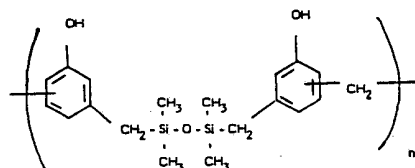
wherein R_1 and R_9 are each lower alkylene groups; $R_2, R_3, R_4, R_{10}, R_{11}$ and R_{12} each are H, OH, CH_3 or CH_2OH ; R_5 to R_8 are each lower alkyl groups, R_{13} is CH_2 or CH_2OCH_2 ; p is 0 or 1; A is phenol or a substituted phenol having substituents in the o, m or p- positions relative to the hydroxyl, or A is:

OH

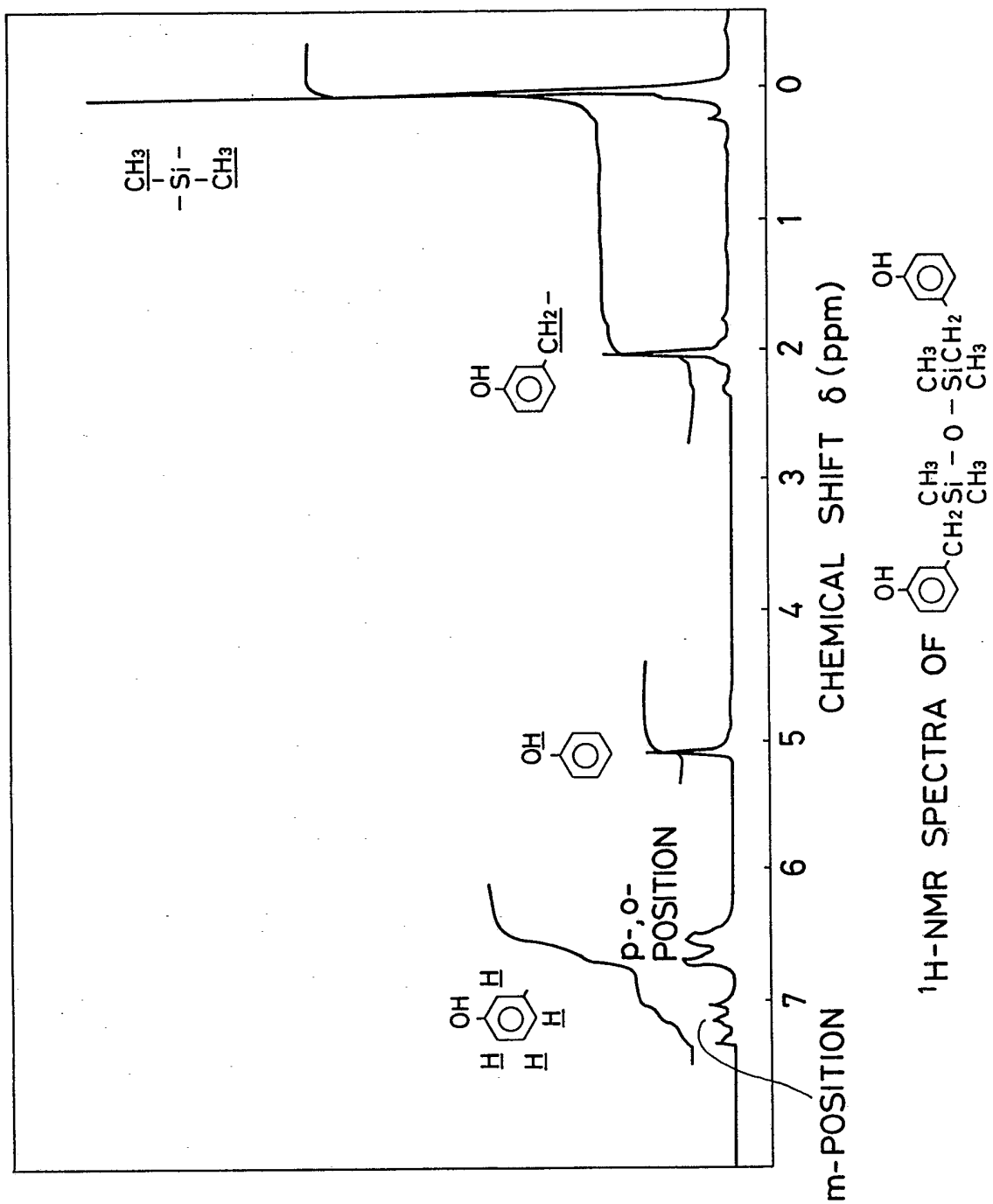


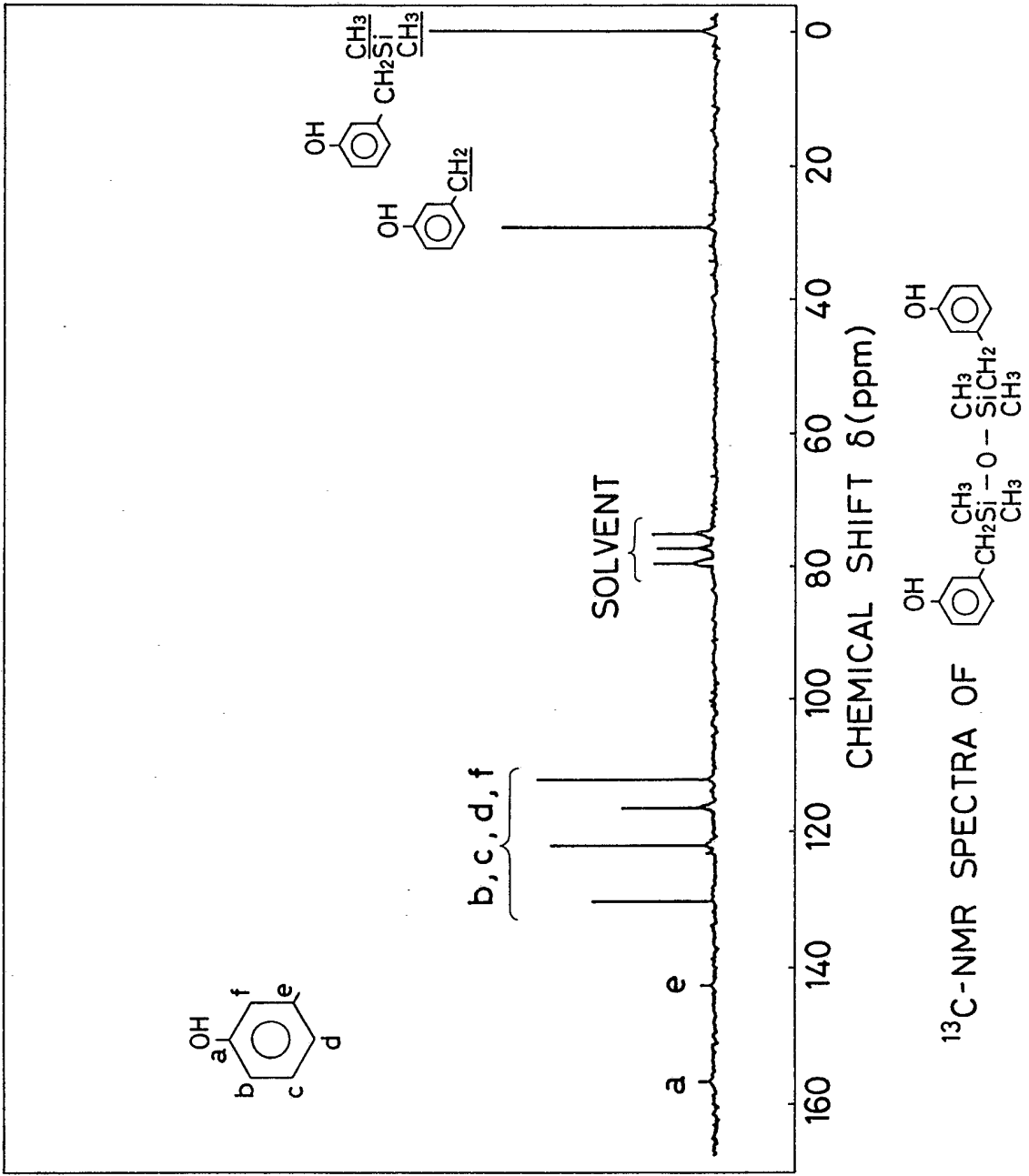
wherein R_{14} is a lower alkylene group; R_{15}, R_{16} and R_{17} are each lower alkyl groups; X is greater than 0 but less than 1; and Y is in the range of 0 to 1-X.

A typical polymer has the formula



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SPECIFICATION

Photoresist materials

5 This invention relates to photoresist materials. Embodiments of the invention are suitable for forming a micropattern applied in the fabrication of semiconductor integrated circuits and magnetic bubble memory elements. 5

In the fabrication of integrated circuits and bubble memory elements, dry etching using a gas plasma, an ion shower, or the like has been used in place of wet etching, since a photoresist pattern prepared by micropatterning can be accurately transferred to a substrate. For this reason, there is a need for a photoresist material having a high resistance to dry etching. 10

In order to obtain a high resolution from such a photoresist material, a three-layered photoresist has been proposed by J M Moran et al, in J. Vac. Sci. Technol., Vol 16, 1620, (1979). The photoresist described there consists of a lower layer of a thick organic film, an intermediate layer of a silicon layer or a silicon oxide layer, and an upper layer of a thin organic film. However, this photoresist requires a complicated and prolonged etching process. 15

If a photoresist material having a good resistance to dry etching when employing, for example, oxygen is used, such material can also serve as the intermediate and upper layers of the three-layered structure. Therefore, the etching process can be considerably simplified.

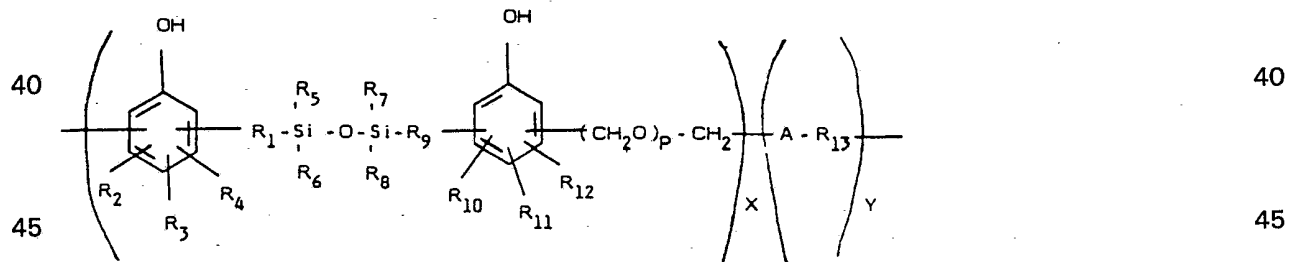
20 Typical examples of such a material are photoresist materials having silicon atoms and described in Japanese patent laid-open applications (Kokai) 60/196750, 60/119550 and 59/208542. 20

However, these photoresist materials are sensitive to electron beams and cannot be used with g-line steppers having a wavelength of 436 nm which presently constitute the most widely used form of exposure apparatus. 25

It is also known that a polydimethylsiloxane has excellent resistance to an oxygen plasma and an etching rate of about 2×10^{-9} m/min. However, this polymer has the drawback that since it is liquid at room temperature, the fluidity of the polymer fails to provide high resolution, and the polymer is thus unsuitable for use as a photoresist material.

30 A polyacetylene-based photodecomposition type positive photoresist material such as a product available from Sanyo Kasei KK has been proposed as a silicon-based photoresist having a g-line absorption property. However, this photoresist material does not have a sufficiently high resolution or high sensitivity since the material is developed with the use of an organic solvent, and the through-put is low. 30

35 According to the present invention there is provided a photoresist material comprising a polymer having at least one recurring unit represented by the following general formula: 35



wherein R_1 and R_9 are each lower alkylene groups;

$R_2, R_3, R_4, R_{10}, R_{11}$ and R_{12} are each H, OH, CH_3 or CH_2OH ;

50 R_5 to R_8 are each lower alkyl groups; 50

R_{13} is CH_2 or CH_2OCH_2 ;

p is 0 or 1;

A is phenol or a substituted phenol having substituents in the o, m or p- positions relative to the hydroxyl, or A is: 55



wherein R_{14} is a lower alkylene group;
 R_{15} , R_{16} and R_{17} are each lower alkyl groups;
 X is greater than 0 but less than 1; and
 Y is in the range of 0 to 1-X.

5 The lower groups referred to may contain up to five carbon atoms. Examples of the phenol derivative referred to as A in the above formula can be o, m and p-cresol, xlenol, and resorcinol. The ratio of X to Y can be arbitrarily determined. However, Y is preferably not more than 0.7 to achieve proper developing properties of the photoresist material with respect to an aqueous solution of an organic base. 5

10 A photoresist material produced with such a composition can have excellent sensitivity to UV light sources such as g and i-lines. Such a photoresist material can be developed with an aqueous solution of an organic base having the same lower swelling power during development as in a positive resist composed of a novolac resin-quinone diazide compound, the most commonly existing photoresist, thereby achieving a high resolution. In a dry etching process 10
 15 using oxygen, the positive photoresist material may comprise a phenol-based, organo-silicon polymer resin and a quinone diazide compound. This positive resist has a higher resistance to etching than the known positive resist which includes a novolac resin. 15

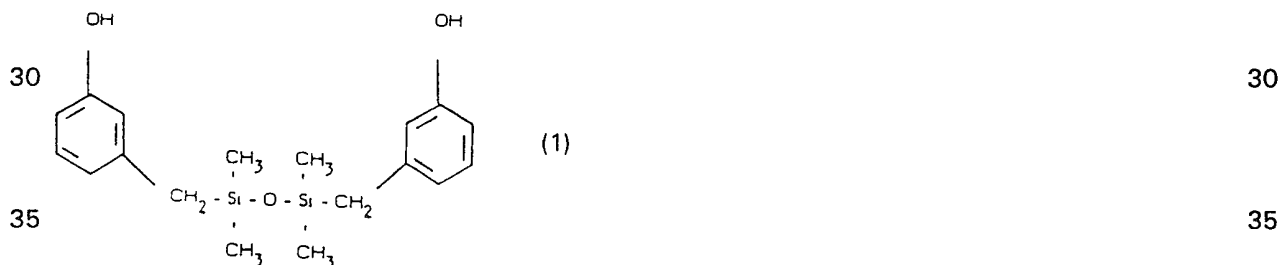
The invention will now be described in more detail, together with a process for the production of the improved photoresist material, by way of examples, and referring to the accompanying drawings, in which: 20

Figure 1 is the $^1\text{H-NMR}$ spectra of the monomers obtained in Examples 1 and 2 described below; and

Figure 2 is a $^{13}\text{C-NMR}$ spectra of the same monomers.

25 *Example 1* 25

The following monomer was prepared, using the synthesis about to be described:



A mixture of 50 g (0.4 mol) of 3-hydroxybenzyl alcohol, 51 g (0.4 mol) of benzyl chloride, 40
 110 g (0.8 mol) of anhydrous potassium carbonate, and 200 ml of anhydrous acetone was refluxed for six hours in a 500 ml three neck distillation flask provided with a reflux condenser. 40
 The resulting benzyl ether compound was extracted with ether and dried with magnesium sulphate to provide a yield of 90%. 30 g (0.14 mol) of the resulting compound was dissolved in carbon tetrachloride. To the resulting solution 16.7 g (0.062 mol) of phosphorus tribromide was 45
 added drop-wise and reacted for more than two hours while the solution was cooled with ice. 45
 The solution was then poured into iced water to decompose the unreacted compounds. The resulting bromide was refined by silica gel chromatography using n-hexane as a developing solvent. The yield was 60%. 1.93 g (0.079 mol) of magnesium and 40 ml of anhydrous ether were charged into a 500 ml three neck distillation flask provided with a nitrogen blowing pipe, a 50
 reflux condenser, and a dropping funnel. 20 g (0.07 mol) of the bromide was dissolved in a 100 ml of anhydrous ether, and the resulting solution was added drop-wise into the flask over a 50
 period of two hours while cooling with ice. After about two additional hours of reaction, 6.6 g (0.07 mol) of dimethylchlorosilane was added drop-wise. The resulting mixture was left to stand at room temperature for about twenty-four hours and then distilled under vacuum (0.6 mmHg), 55
 boiling point of 140°C). The yield was 60%. 55

5 g (0.019 mol) of the resulting distilled product was added drop-wise into ethanol in which 100 mg of a 5% palladium-carbon catalyst was dispersed. After the addition, 200 mg of the 5% palladium-carbon catalyst and several drops of concentrated hydrochloric acid were added to effect hydrogenation. The resulting product was refined using silica gel chromatography with n-hexane as the developing solvent to obtain a monomer represented by formula (1). The yield 60
 was about 100%. 60

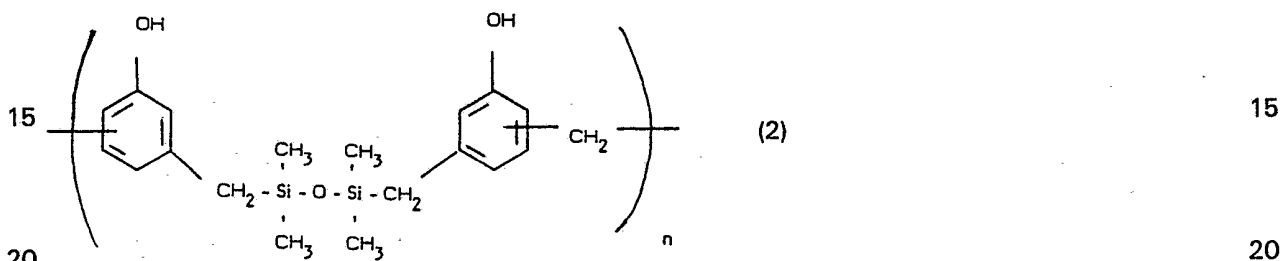
The analytical values of the monomer are summarized as follows: Infra-red absorption spectrum (cm^{-1}): 3350 (-OH); 2950 (CH_2 -); 1250, 850, ($\text{Si}-(\text{CH}_3)_3$); 1050 (Si-O-Si).
 $^1\text{H-NMR}$ spectrum (δ) ppm: 0.04 (12H, S, $-\text{CH}_3$ Si-); 2.08 (4H, S, $-\text{CH}_2$ -); 5.16 (2H, S, -OH); 6.4 to 7.4 (8H, m, benzene nucleus) (see Fig. 1). 65

^{13}C -NMR spectrum (see Fig. 2).

Precision molecular weight: calculated, 346.1447; found, 346.1474.

If a compound having substituent groups in the benzene nucleus is used in place of 3-hydroxybenzyl alcohol in the synthesis of the above monomer, the corresponding monomer can be obtained.

5.4 g (0.0156 mol) of the siloxane-based phenol monomer represented by the formula (1), 1.14 g of formalin (37% aqueous solution), 6 g of ethyl cellosolve acetate, and 27 mg of oxalic acid dihydrate were placed in a 100 ml flask and were heated and stirred at 110°C for eight hours. The resulting product was washed with water and refined under vacuum to obtain a polymer photoresist material represented by:



The molecular weight of the photoresist material measured according to gel permeation chromatography using a monodispersed polystyrene as a reference was $\bar{M}_w=5200$ and $\bar{M}_n=1100$, with a ratio $\bar{M}_w/\bar{M}_n=4.75$.

Example 2

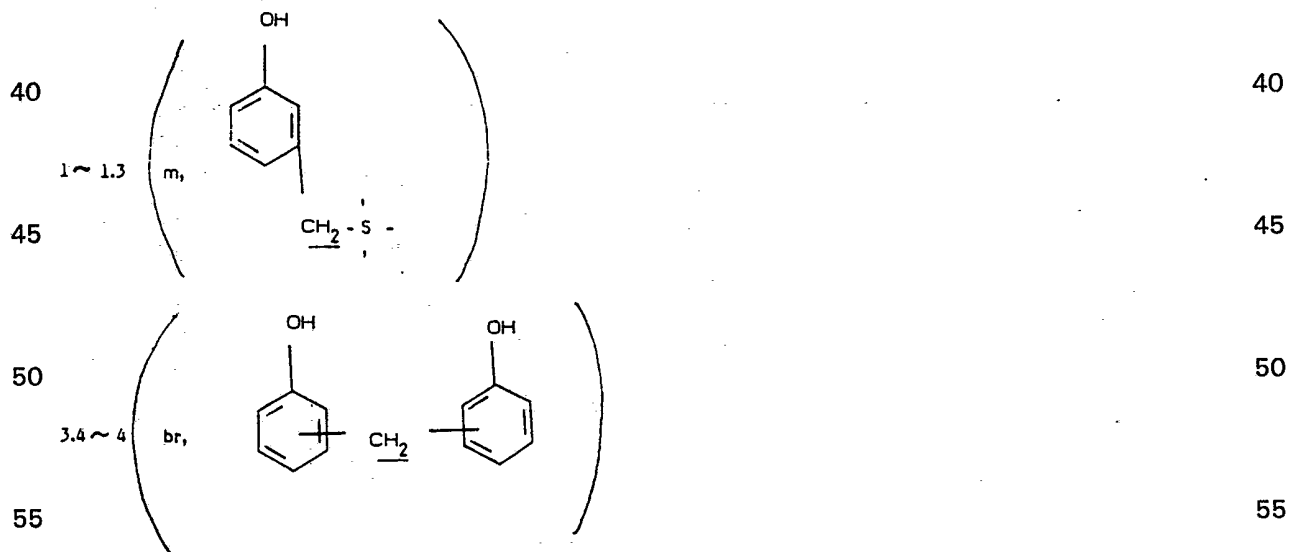
Following the same procedure as in Example 1, except using a heating and stirring time of fourteen hours instead of eight hours, a new photoresist material was obtained. The molecular weights of the photoresist material measured in the same manner as in Example 1 were

$\bar{M}_w=28300$ and $\bar{M}_n=2200$ with a ratio $\bar{M}_w/\bar{M}_n=12.9$.

The analytical values of the polymers obtained in Examples 1 and 2 are summarized as follows:

Infra-red absorption spectrum (cm^{-1}): 3300 ($-\text{OH}$); 2950 ($-\text{CH}_2-$); 1250, 850 ($-\text{Si}(\text{CH}_3)_2-$); 1050 ($-\text{Si}-\text{O}-\text{Si}-$).

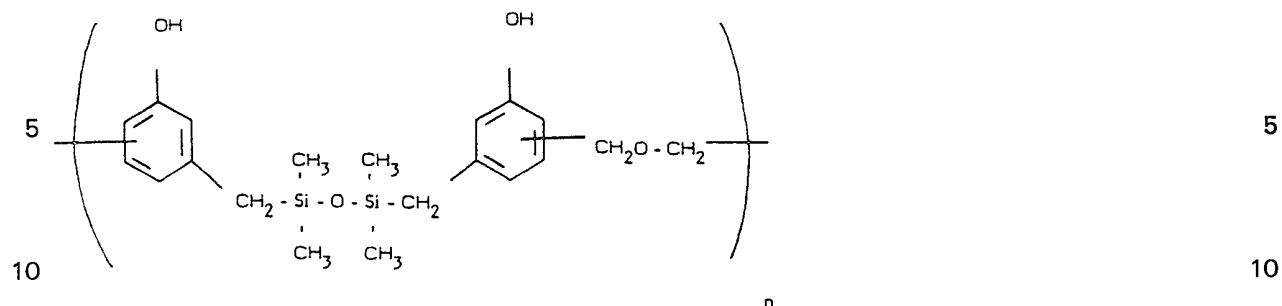
^1H -NMR spectrum (δ) ppm: 0.04 to 0.2 (br, $\text{S}-\text{CH}_3$);



6.2 to 6.8 (br, benzene nucleus).

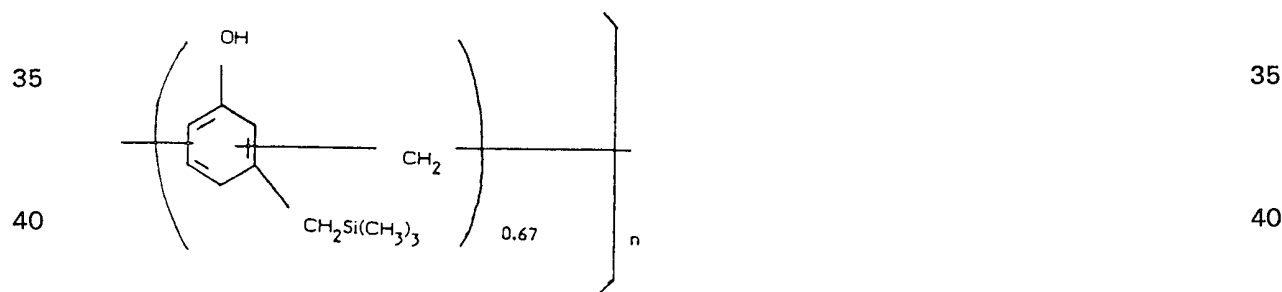
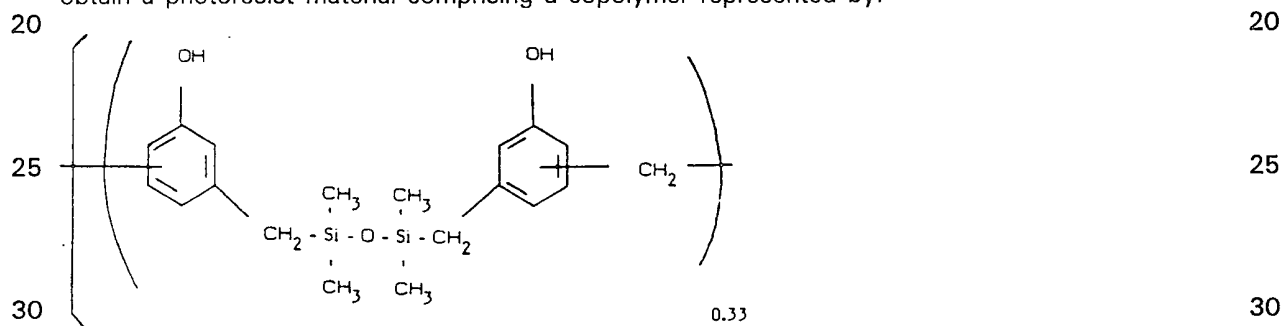
In Examples 1 and 2, a small amount of a polymer having a recurring unit with a methylol group introduced into the benzene nucleus of the polymer represented by formula (2) was also produced.

In Examples 1 and 2, when the polymerization reaction is performed in an alkaline solvent, a polymer represented by the following formula can be mainly produced in place of the polymer represented by formula (2):



Example 3

15 6 g (0.033 mol) of m-trimethylsilylmethylphenol, 5.71 g (0.0165 mol) of the siloxane-based phenol monomer obtained in Example 1 and represented by formula (1), 3.61 g of a 37% aqueous solution of formalin, 13 g of ethyl cellosolve acetate, and 87 mg of oxalic acid dihydrate were placed in a 100 ml flask and heated and stirred at 110°C for thirteen hours to obtain a photoresist material comprising a copolymer represented by:



45 Following the same procedure as in Example 1, the molecular weights of the photoresist material were measured to be $M_w=5000$ and $M_n=2000$, with a ratio $M_w/M_n=2.5$. The analytical values of the copolymer were similar to those in Example 1.

The resistance of the polymers obtained in Examples 1 and 3 to reactive etching using oxygen was compared with the resistance of 'Microposit 1400' a commercial material widely used and available from Shipley Inc. The following results were obtained:

50

	Etching Rate ($\times 10^{-10}$ m/min)
Polymer of Example 1	78
Polymer of Example 3	66
Commercially available product	1250

55

The etching was effected under an oxygen partial pressure of 10 mmHg, an oxygen flow rate of 50 SCCM, and an RF output of 0.1 W/cm².

The polymers obtained in Examples 1 to 3 thus have a higher resistance to etching using oxygen. The M_w values of the polymers range from about 3000 to about 30000.

60 The 'Microposit 1400' was spin-coated on a silicon substrate to form a 2 μ m thick photoresist film. The photoresist film was baked on a hotplate at 200° for twenty minutes. A cellosolve acetate/xylene solution of the polymer obtained in Example 1 and combined with 15% by weight of a sensitizer (a quinone diazide compound) was spin coated on the 2- μ m thick photoresist film. The film was dried at 80°C for twenty minutes to obtain a two-layered photoresist structure.

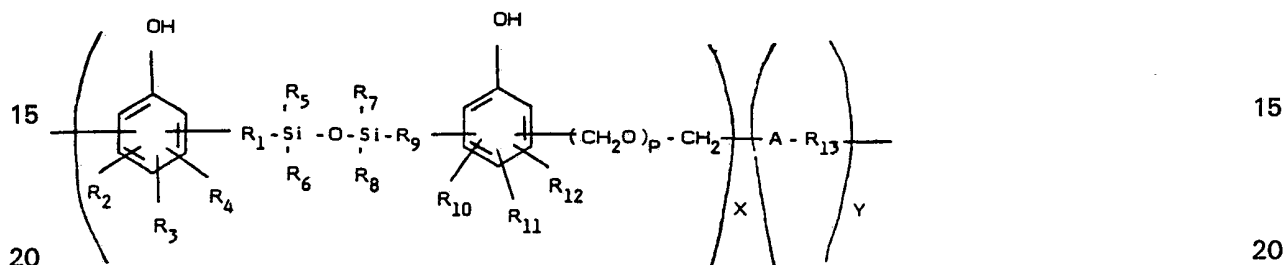
65 This structure was developed with a 5% aqueous solution of tetramethylammonium hydroxide.

The substrate was etched by reactive sputter etching apparatus under the above etching conditions. As a result, a 0.6- μm pattern was formed with sharp edges. No pattern transfer difference was observed when the pattern was transferred onto a thick organic layer.

- 5 Suitable sensitizers for the above polymers include o-benzoquinone diazide, o-naphthoquinone diazide and p-benzoquinone diazide. 5

CLAIMS

1. A photoresist material comprising a polymer having at least one recurring unit represented by the following general formula: 10



wherein R_1 and R_9 are each lower alkylene groups;
 R_2 , R_3 , R_4 , R_{10} , R_{11} and R_{12} are each H, OH, CH_3 or CH_2OH ;

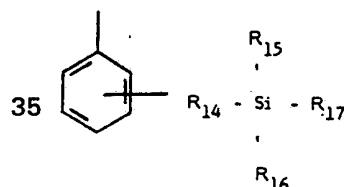
R_5 to R_8 are each lower alkyl groups;

25 R_{13} is CH_2 or CH_2OCH_2 ;

p is 0 or 1;

A is phenol or a substituted phenol having substituents in the o, m or p- positions relative to the hydroxyl, or A is:

30 OH



wherein R_{14} is a lower alkylene group;

40 R_{15} , R_{16} and R_{17} are each lower alkyl groups;

X is greater than 0 but less than 1; and

Y is in the range of 0 to $1-X$.

2. A photoresist material according to claim 1 wherein Y is not more than 0.7.
 3. A photoresist material according to claim 1 or claim 2 wherein R_1 , R_9 and R_{14} are each alkylene groups containing 1 or 2 carbon atoms. 45

4. A photoresist material according to claim 3 wherein R_5 to R_8 are each alkyl groups containing from 1 to 5 carbon atoms.

5. A multi-layer photoresist structure wherein at least one layer is composed of a material according to any of the preceding claims wherein said layer also contains a quinone diazide sensitizer. 50

6. A photoresist material substantially as hereinbefore described with reference to Example 1.
 7. A photoresist material substantially as hereinbefore described with reference to Example 2.
 8. A photoresist material substantially as hereinbefore described with reference to Example 3.