

PHOTORESIST COMPOSITIONS COMPRISING STYRYL COMPOUNDS

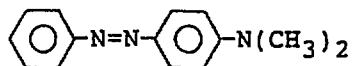
The present invention relates to

photoresist compositions comprising styryl compounds, which photoresist compositions can be preferably used to form fine patterns on a substrate having high reflectance in the production of semiconductors.

A photoresist which comprises a sensitizing compound having a quinone diazide group and a novolak resin, or which comprises a bisazide sensitizer and a cyclized rubber is used in the production of integrated circuits such as LSI.

In a process for producing the integrated circuits, fine patterns are formed on various substrates through photoresists. However, when the conventional photoresists are used on the substrates having high reflectance such as those made of aluminum, aluminum-silicon, polysilicon and the like, various problems arise. For example, a region which should not be exposed may be exposed because of reflection on a surface of the substrate and/or side walls of steps. This phenomenon is generally called as notching or halation.

To solve these problems and prevent deterioration of resolution, Japanese Patent Publication No. 37562/1976 proposes a photoresist composition which comprises, as a light absorber, a dye represented by the formula:



having characteristic absorptions in the ultraviolet range (Oil Yellow [C.I. 11020]). This photoresist composition can decrease light transmission through the photoresist layer and reduce the undesirable exposure of the substrate.

In the context of the specification, a "photoresist" is intended to mean a composition which comprises a sensitizer and a resin such as novolak, and a "photoresist composition" is intended to mean a composition which comprises a "photoresist" and a light absorber.

In general, if the light absorber is added to the photoresist, undesirable problems may arise. For example, photoresist drastically loses its sensitivity and productivity of the semiconductors is decreased.

The photoresist layer is usually formed by applying the photoresist composition containing a solvent on a wafer and prebaking the wafer with the applied photoresist composition to evaporate off the solvent. However, some light absorbers may precipitate during storage of the photoresist composition, or sublime during prebaking so that a concentration of the light absorber in the

photoresist layer formed on the wafer may be lowered, which lead to unsatisfactory results or variation of quality of the produced semiconductors.

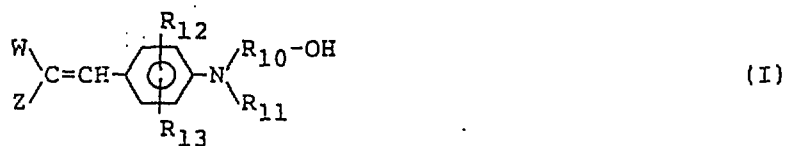
To solve these problems, phenylazobenzene derivatives are proposed in Japanese Patent Kokai (Laid-open) Publication Nos. 368358/1980 and 174941/1983. But, the use of such derivatives creates some problems. For example, the phenylazobenzene derivatives should be used in a large amount in order to obtain sufficient absorption at desired wavelength, especially when the prebaking temperature is raised, or such derivatives have inferior anti-sublimation, a broad absorption range, low absorbing performance and undesirable absorption at certain wavelength. Japanese Patent Kokai Publication No. 93445/1986 discloses a photoresist composition comprising, as a light absorber, a certain styryl compound. Although the disclosed styryl compound can solve the problems associated with the prebaking, it greatly decreases the sensitivity of the photoresist.

An object of the present invention is to provide a photoresist composition suitable for forming fine patterns having high resolution on a substrate having high reflectance without causing any halation or notching.

A further object of the present invention is to provide a photoresist composition which is stable against the prebaking of the substrate and suffers from less deterioration of sensitivity caused by the addition of the light absorber.

As the result of the extensive study, it has been found that photoresist compositions comprising the styryl compound of the following formula (I) accomplish the above objects and solve the problems associated with the prior arts. The present invention has been completed based on this finding.

According to the present invention, there is provided a photoresist composition which comprises a compound of the general formula:

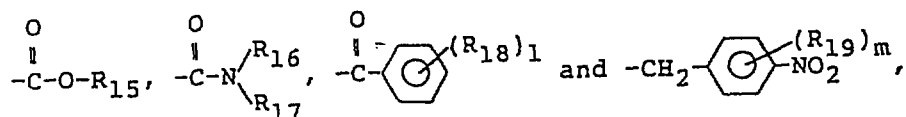


wherein W and Z are the same or different and an electron attractive group; R_{10} is an optionally substituted $\text{C}_1\text{-C}_{10}$ alkylene group, R_{11} is a hydrogen atom, an optionally substituted $\text{C}_1\text{-C}_{10}$ alkyl, alkenyl or aralkyl group; and each of R_{12} and R_{13} is a hydrogen atom, an optionally substituted lower alkyl group, an optionally substituted lower alkoxy group, an amide group or a halogen atom.

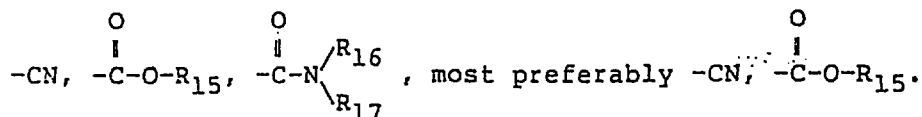
The compound of the formula (I) is added to a photoresist to prepare the photoresist composition of the present invention. Any conventional positive or negative photoresist can be used according to the present invention. A photoresist which comprises a novolak resin and a naphthoquinone diazide compound is preferably used. The novolak resin is obtained through the addition condensation reaction of a phenol compound with formaldehyde.

Also, a photoresist which comprises a cresol novolak resin and an ester of polyhydroxybenzophenone with naphthoquinone-1,2-diazide sulfonic acid is preferably used. The cresol novolak resin can be prepared by a reaction of meta-cresol and/or para-cresol with formalin, or a reaction of meta-cresol, para-cresol and 3,5-xyleneol with formalin. Examples of the polyhydroxybenzophenone are 2,3,4-trihydroxybenzophenone, 2,3,4,4'-tetrahydroxybenzophenone, 2,2',4,4'-tetrahydroxybenzophenone, 2,3,3',4-tetrahydroxybenzophenone, 2,2',3,4,5-pentahydroxybenzophenone, 2,3,3',4,5-pentahydroxybenzophenone, 2,3,3',4,4'-pentahydroxybenzophenone, 2,2',3,4,4'-pentahydroxybenzophenone, and 2,2',3,3',4-pentahydroxybenzophenone.

In the general formula (I), W, Z, R₁₀, R₁₁, R₁₂ and R₁₃ are as defined above. Each of W and Z is preferably -CN,



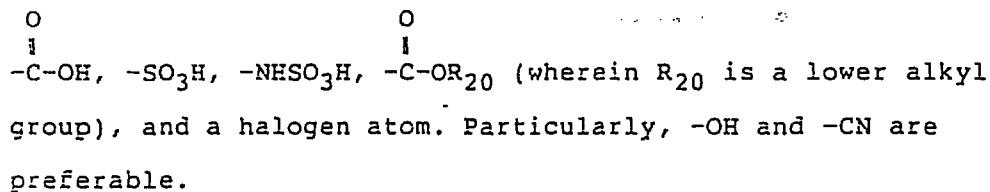
more preferably



R₁₀ is preferably an optionally substituted C₁-C₈ alkylene group, R₁₁ is preferably an optionally substituted lower alkyl, alkenyl or aralkyl group, and each of R₁₆ to R₁₉ is a hydrogen atom, an optionally substituted lower alkyl group or a phenyl group.

Each of 1 and m represents a number of 1 to 2.

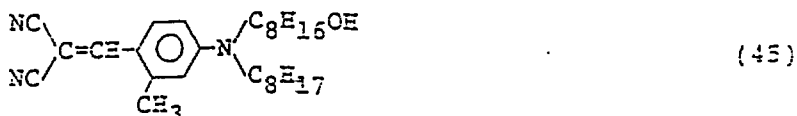
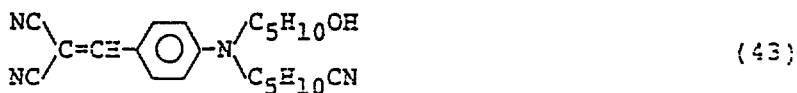
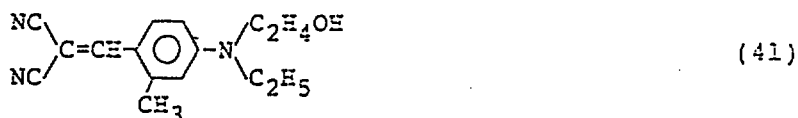
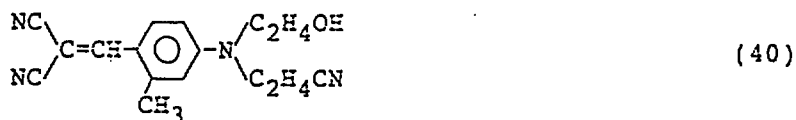
Examples of the substitutes which is optionally bonded to the above groups are -OH, -CN,

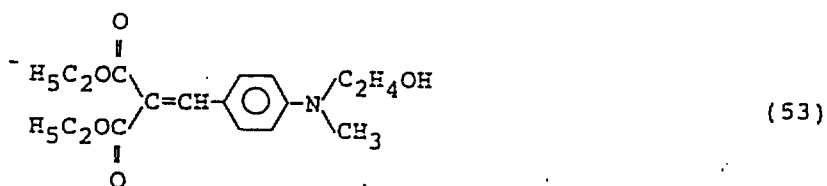
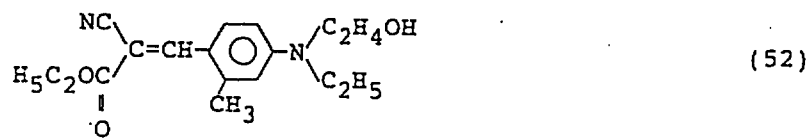
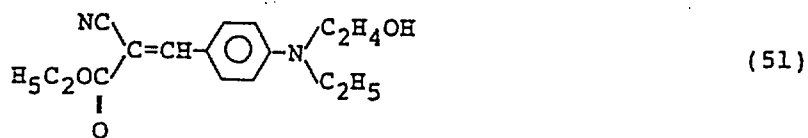
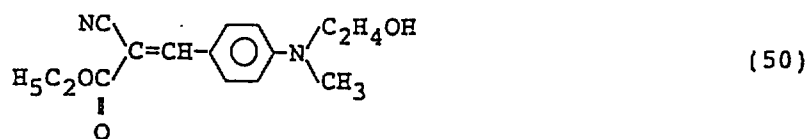
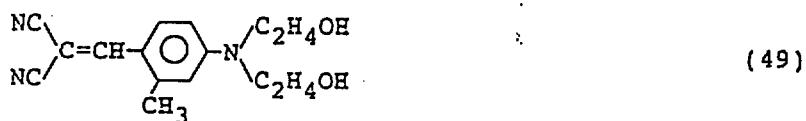
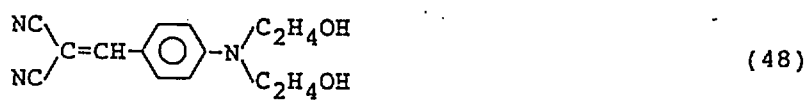
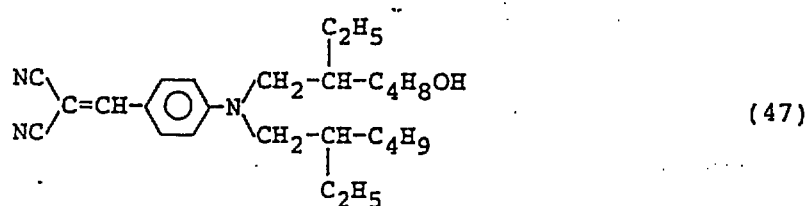
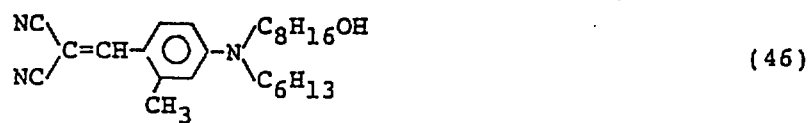


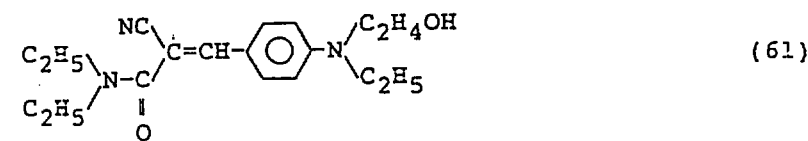
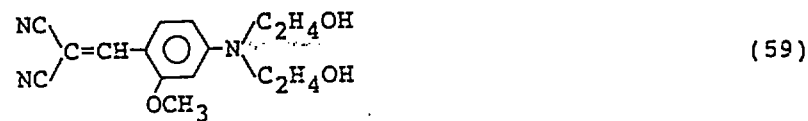
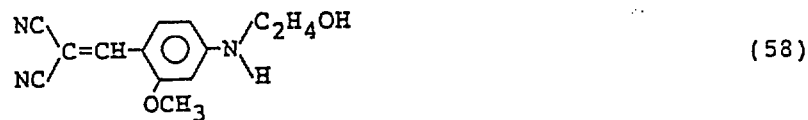
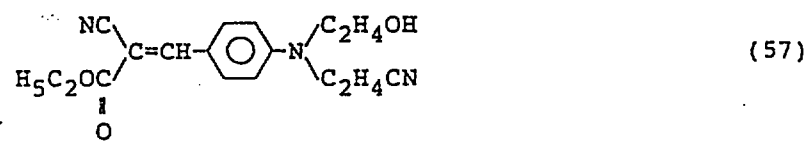
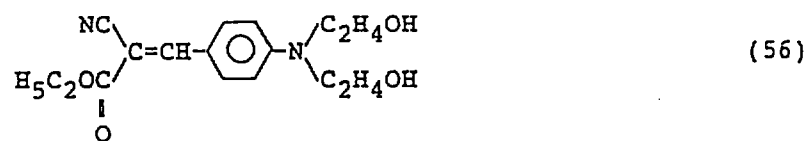
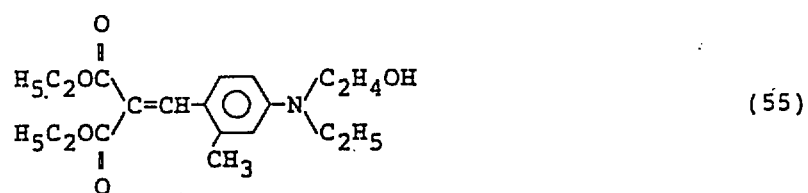
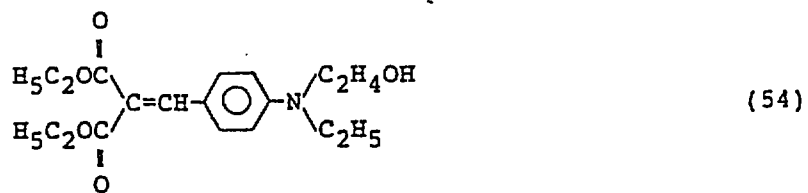
In this specification, the "lower" used in connection with the alkyl or alkoxy group or other groups is intended to mean that the group contains 1 to 10 carbon atoms, preferably 1 to 8 carbon atoms.

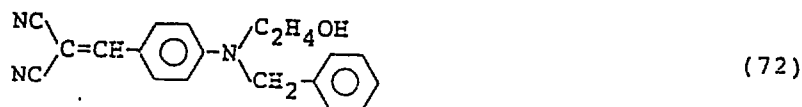
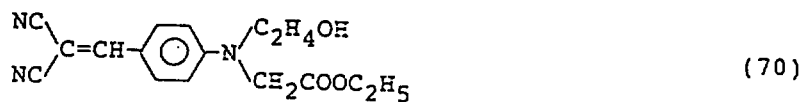
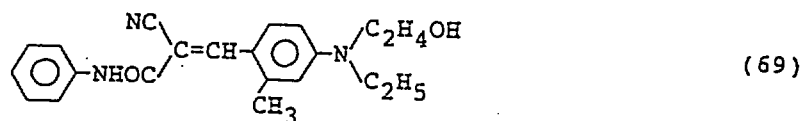
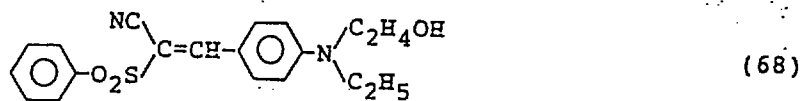
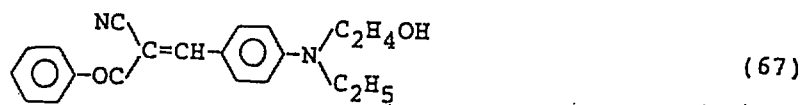
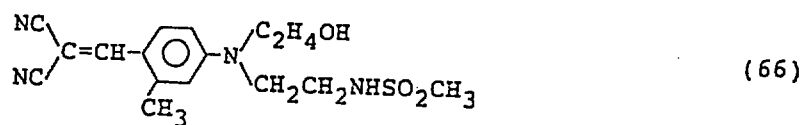
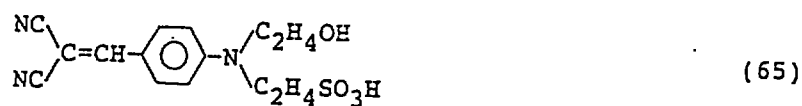
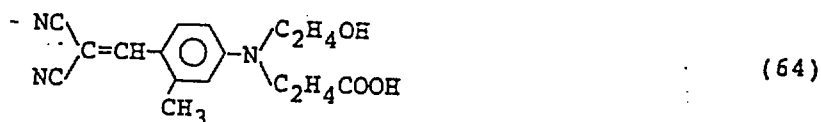
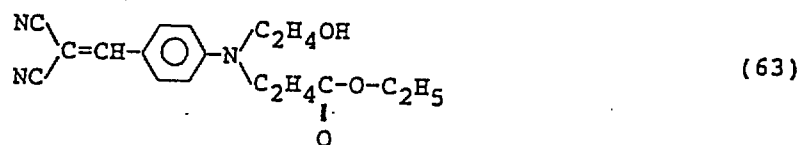
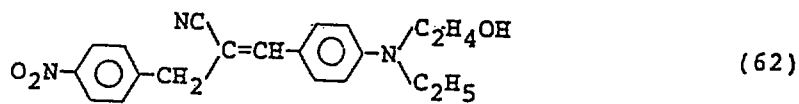
Most of the compounds of the formula (I) are known from U.S. Patent No. 4,439,372 or J. of the Society of Dyers and Colourists, April (1977) 126-133. Then, the compounds (I) can be easily prepared by the method described in the above literatures or analogous methods thereto. Among the compounds (I), those having the maximum absorption in a wavelength range not longer than 550 nm, particularly between 350 nm and 400 nm are preferably used in the photoresist composition.

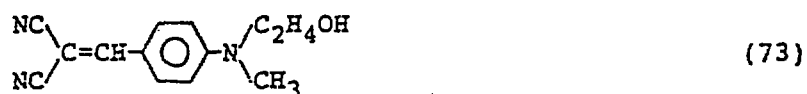
Examples of the compounds (I) which are suitable as the light absorber in the photoresist composition are as follows. These examples will not limit the scope of the present invention.











The amount of the compound (I) to be added to the photoresist composition is from 0.1 to 20 %, preferably from 0.2 to 10% based on the weight of the solid component in the photoresist. If the amount of the compound (I) is smaller than the above lower limit, the photoresist composition cannot prevent the halation sufficiently. If the amount of the compound (I) exceeds the above upper limit, the photoresist composition tends to have inferior profile or sensitivity. The photoresist composition may optionally contain at least one other dye compound.

The photoresist composition may optionally contain at least one other light absorber.

As described above, the compound (I) is prepared by the known processes. The typical processes are as follows:

(1) An amine is subjected to formylation according to the Vilsmeier reaction and then reacted with an active methylene component to obtain the compound (I).

(2) An amine is converted to a Schiff base and then reacted with an active methylene component to obtain the compound (I).

In the process (1) or (2), to suppress side reactions and improve a yield of the desired product, prior to the formylation in the process (1) or the conversion to the Schiff base, an active group in the amine is protected through esterification, and the esterified active group is

hydrolyzed before or after the reaction with the active methylene component.

The styryl compounds of the formula (I).
are easily dissolved in organic solvents such as xylene, ethyl cellosolve, cyclohexanone, cellosolve acetate, and butyl acetate. These styryl compounds have good compatibility with the rubber base photoresists and also deep U.V. resists. Because the styryl compounds do not sublime even at high temperatures, a photoresist composition which comprises the compound (I) can be pre-baked at high temperatures to remove the solvent completely so that the uniform photoresist layer can be formed on the substrate. In addition, since the photoresist composition according to the present invention has good antihalation effect, fine patterns can be formed on the substrate with good reproducibility.

Since styryl compounds used in the present invention do not precipitate even after long storage, an uneven coating due to the precipitation can be prevented.

With the photoresist compositions according to the present invention, the problems associated with the prior arts can be solved, and patterns with high resolution can be

formed on the substrate having high reflectance.

The present invention will be illustrated more in detail with the following examples, but it is not limited to these examples.

Reference Example 1

(synthesis of the light absorber)

A mixture of 16.5 g (0.1 mol) of (N-ethyl-N-hydroxyethyl)aniline, 0.5 ml of pyridine and 12.3 g of acetic anhydride was stirred for 20 hours at 40-50°C.

After cooling the mixture down to 20-23°C, 5 ml of methanol was added to the mixture and then stirred for 1 hour. The resulting mixture was extracted three times with 500 ml of water and 200 ml of ethyl acetate.

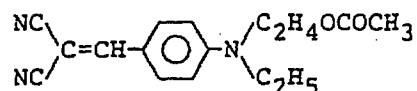
Thereafter, the upper layer was filtered, and the filtrate was concentrated to obtain 20.7 g of (N-ethyl-N-acetoxyethyl)aniline.

20.7 Grams of (N-ethyl-N-acetoxyethyl)aniline thus obtained was dissolved in 25 ml of DMF (dimethylformamide). 13.5 Milliliters of phosphorus oxychloride were dropwise added over 12 minutes at about 40°C while stirring. The mixture was stirred for 6 hours at 60°C and thereafter allowed to cool down to 30°C. Then the solution was poured into 100 ml of ethanol.

Then 30 ml of a 25 % aqueous ammonia solution and 6.6 g of malonic nitrile were added, and the condensation reaction was carried out for 5 hours at 70°C while refluxing.

After cooling down to 10-20°C, the resulting precipitate was filtered off.

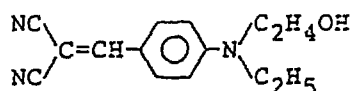
The filtrate contained about 50 % of a compound of the formula.



The filtrate was added to 40 ml of ethanol and the resulting mixture was heated at 75°C while stirring. Then 15 ml of 37 % hydrochloric acid was poured. The mixture was then reacted for 30 minutes under reflux conditions.

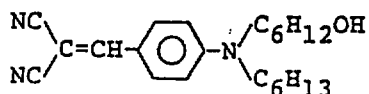
Thereafter the solution was allowed to cool down to about 60°C, and then poured in iced water to precipitate crystal.

The resulting crystal was filtered, washed with water and dried to obtain 19.2 g of 4-(N-ethyl-N-hydroxyethyl)amino- α,α -dicyano styrene of the formula:

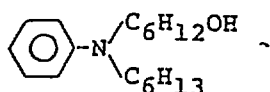


Reference Example 2

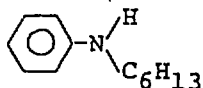
About 17.5 g of 4-(N-hexyl-N-hydroxyhexyl)amino- α,α -dicyanostyrene of the formula:



was obtained by the same procedures as in Reference Example 1 except that an amino compound of the formula:



which had been obtained by the reaction of 0.1 mol of a compound of the formula:



with $\text{Cl}(\text{CH}_2)_6\text{OH}$, was used in place of 16.5 g of (N-ethyl-N-hydroxy ethyl)aniline.

Examples 1 to 3

Into PF-6200 (manufactured by Sumitomo Chemical Company, Limited; a solid content of 31.0 % by weight), which comprises a novolak resin ($\text{Mw} = 12,000$) prepared mainly from m-cresol and at least one compound having o-quinone diazide groups, each of the compounds shown in Table 3 was added to prepare photoresist compositions.

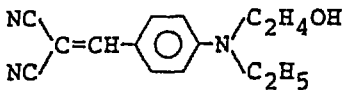
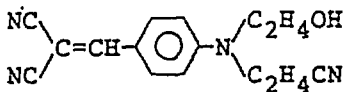
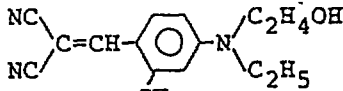
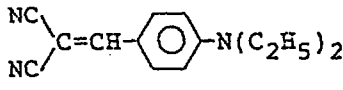
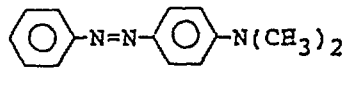
The amount of the compound was 0.68 % by weight based on the solid amount in PF-6200.

Each of the photoresist compositions was coated on a 4 inch silicon wafer with an aluminum film on its surface by means of a spinner so as to form a resist film of 1.80 μm in thickness.

The coated silicon wafer was baked for 1 minute on a hot plate kept at 100°C, and exposed and exposed to light through a test reticule while varying the exposure value stepwise by means of a reduced projection exposing apparatus (Nicon NSR-1505G). Thereafter, the silicon wafer was developed by a static paddle method for 60 seconds at 23°C in a developing solution SOPD (manufactured by Sumitomo Chemical Company, Limited) by means of an automatic developing machine.

The results are shown in Table 1.

Table 1

No.	Chemical structure	Relative sensitivity	Absorbance ratio
Example 1		0.6	0.97
Example 2		0.6	0.98
Example 3		0.6	1.0
Comparative Example 1		1.0	0.95
Comparative Example 2		1.9	0.75

As understood from the results in Table , patterns with high sensitivity were formed in Examples of the present invention.

The pattern could be resolved sharply even when the line width was 0.8 μm . No notching caused with the reflected light on the side surfaces of patterns was found. The above results indicate that the photoresist compositions of the present invention impart excellent antihalation effect.

The same compositions were coated on a glass wafer in the same procedures as in case of the aluminum wafer described above.

The glass wafer was prebaked for 30 minutes in a convection oven kept at 120°C, and the absorbance ratio at 436 nm was measured with an UV-visible spectrum meter (comparison with that before prebaking). The effect of decomposition of the sensitizer was neglected. The results showed that the absorbance ratio was about one (1), which indicates that the photoresist compositions of the present invention are excellent in antisublimation.

A silicon wafer was exposed in the same way as above and after-baked for 30 minutes in a convection oven kept at 90°C. After 4 days storage at room temperature, the silicon wafer was developed.

Inspection on deposits remained between patterns revealed that no precipitation was found.

After 6 months storage at 23°C, no light absorber precipitated in the resist composition.

On the contrary, the photoresist compositions of Comparative Examples had insufficient sensitivity and anti-sublimation.

Example 4 and Comparative Example 3

In these Examples, used was a meta-cresol novolak resin characterized in that the area ratio in the gel permeation chromatographic pattern (GPC pattern) was as follows:

A range wherein the molecular weight is larger than 150 and less than 500 (not including a phenol and the

unreacted monomer) was 18.2 %, a range wherein the molecular weight is more than 500 and less than 5,000 was 20.8 % and a range wherein the molecular weight exceeds 5,000 is 61.0 %.

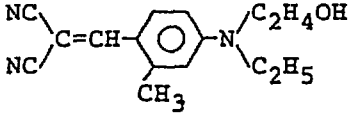
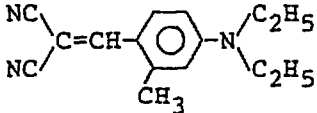
In the same way as described in European Patent Publication No. 271199, 17 parts (by weight) of the novolak resin, 5.25 parts of a condensation product of napthoquinone-(1,2)-diazide-(2)-5-sulfonic acid chloride with 2,3,4-trihydroxybenzophenone and 0.15 parts of each compound shown in Table 2 were dissolved in 49.25 parts of ethyl cellosolve acetate.

The mixture was filtrated through a 0.2 μ m filter to obtain a photoresist composition.

On a silicon wafer on which aluminum had been deposited in a thickness of 1 μ m, the photoresist composition was coated by means of a spin coater. Then the coated silicon wafer was baked for 1 minute on a hot plate kept at 100°C. The photoresist film thickness after bake was 1.28 μ m.

Thereafter, patterns were formed in the same way as in Example 1. These results are summarized in Table 2.

Table 4

No.	Chemical structure	Relative sensitivity
Example 4		0.6
Comparative Example 3		1.0

As understood from the results in Table 2, the photoresist composition of Example 4 of the present invention imparted high sensitivity, and the formed patterns could be resolved sharply even when the line width was 0.7 μm .

No notching due to reflected light on the side surfaces of the patterns or no distortion of the patterns could be found, and excellent antihalation effect was achieved.

In addition, excellent antishlimation was also achieved and no deposit of the light absorber could be found.

Examples 5 to 8

Patterns were formed on an aluminum wafer by the same procedures as in Example 4 except that each compound in Table 3 was used.

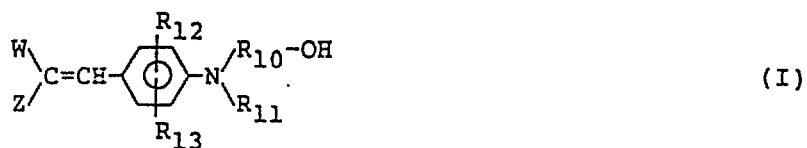
Table 5

No.	Chemical structure
Example 5	$\begin{array}{c} \text{NC} \\ \diagdown \\ \text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{N} \begin{array}{l} \diagup \text{C}_6\text{H}_{12}\text{OH} \\ \diagdown \text{C}_6\text{H}_{13} \end{array} \\ \diagup \\ \text{NC} \end{array}$
Example 6	$\begin{array}{c} \text{NC} \\ \diagdown \\ \text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{N} \begin{array}{l} \diagup \text{C}_2\text{H}_4\text{OH} \\ \diagdown \text{C}_2\text{H}_4\text{OH} \end{array} \\ \diagup \\ \text{NC} \end{array}$
Example 7	$\begin{array}{c} \text{NC} \\ \diagdown \\ \text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{N} \begin{array}{l} \diagup \text{C}_4\text{H}_8\text{OH} \\ \diagdown \text{C}_4\text{H}_9 \end{array} \\ \diagup \\ \text{NC} \end{array}$
Example 8	$\begin{array}{c} \text{NC} \\ \diagdown \\ \text{C}=\text{CH}-\text{C}_6\text{H}_4-\text{N} \begin{array}{l} \diagup \text{C}_2\text{H}_4\text{OH} \\ \diagdown \text{C}-\text{O}-\text{C}_2\text{H}_5 \\ \quad \quad \quad \text{O} \end{array} \\ \diagup \\ \text{NC} \end{array}$

In each Example, the relative sensitivity is as high as 0.5 to 0.7, and the formed patterns could be resolved sharply even when the line width was 0.7 μm . No notching due to the light reflection on the side surfaces of the patterns was found. The antisublimation was good and no precipitation of the light absorber was found.

CLAIMS:

1. A photoresist composition which comprises a compound of the general formula:



wherein W and Z are the same or different and an electron attractive group; R₁₀ is an optionally substituted C₁-C₁₀ alkylene group, R₁₁ is a hydrogen atom, an optionally substituted C₁-C₁₀ alkyl, alkenyl or aralkyl group; and each of R₁₂ and R₁₃ is independently a hydrogen atom, an optionally substituted lower alkyl group, an optionally substituted lower alkoxy group, an amide group or a halogen atom.

