

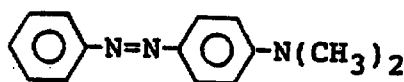
Description

The present invention relates to styryl compounds, a process for preparing said styryl compounds and photoresist compositions comprising said 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 novel styryl compound which is useful as a light absorber in the photoresist composition suitable for micro-lithography.

Another object of the present invention is to provide a process for preparing the novel styryl compound.

A further object of the present invention is to provide a light absorber which does not sublime during prebaking of a photoresist composition applied on a substrate or does not precipitate during storage of the composition and has good compatibility with a photoresist.

A yet another 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.

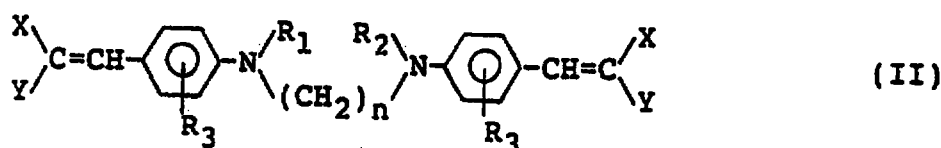
A yet further object of the present invention is to provide a photoresist composition which is stable against the prebaking of the substrate and suffers from less deterioration of sensitivity caused by the addition of the light absorber.

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

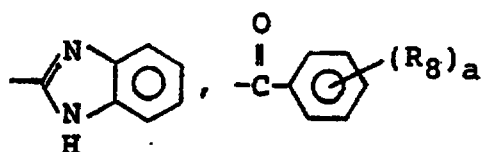
According to the first aspect of the present invention, there is provided a compound of the general formula:



or



wherein R_1 and R_2 are the same or different and a hydrogen atom, an optionally substituted alkyl group, an optionally substituted alkenyl group or an optionally substituted aralkyl group or R_1 and R_2 may form a ring together with the nitrogen atom to which they are bonded, which ring may include at least one hetero atom in addition to said nitrogen atom; R_3 is $-\text{OH}$, $-\text{OCOR}_5$ or $-\text{OSi}(\text{R}_5)_3$; X and Y are the same or different and are $-\text{CN}$, $-\text{COOR}_4$, $-\text{CONR}_6\text{R}_7$,



or

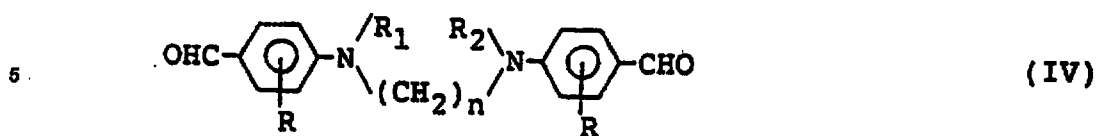


R_4 and R_5 are each an alkyl group; R_6 , R_7 , R_8 and R_9 are the same or different and a hydrogen atom, an optionally substituted lower alkyl or phenyl group; n is a number of 2 to 15; and a and b are the same or different and a number of 1 to 2.

According to the second aspect of the present invention there is provided a process for preparing the compound of the general formula (I) or (II), which comprises reacting a compound of the general formula:



or



10 wherein R_1 , R_2 and n are same as defined above; and R is $-\text{OCOR}_5$ or $-\text{OSi}(\text{R}_5)_3$ with a compound of the general formula:

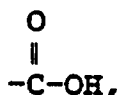


wherein X and Y are same as defined above.

20 According to the third aspect of the present invention, there is provided a photoresist composition which comprises the compound of the general formula (I) or (II).

In the general formulae (I) and (II), preferably, each of R_1 and R_2 is a hydrogen atom or an alkyl, alkenyl or aralkyl group which has up to 10 carbon atoms, particularly up to 8 carbon atoms and may optionally has at least one substituent. Examples of the substituent are $-\text{OH}$, $-\text{CN}$,

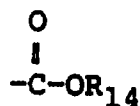
25



30

$-\text{SO}_3\text{H}$, $-\text{NHSO}_3\text{H}$,

35



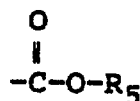
(in which R_{14} is a lower alkyl group) or a halogen atom such as fluorine, chlorine, bromine or iodine. Among the substituents, $-\text{OH}$ and $-\text{CN}$ are preferable.

40

Each of R_4 and R_5 is preferably a C_1 - C_4 alkyl group. n is preferably a number of 3 to 9.

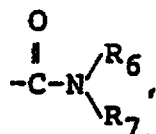
Each of X and Y is preferably $-\text{CN}$,

45



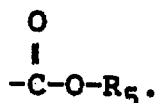
and

50



55

particularly -CN and



The compound (I) may be prepared by a condensation reaction of the compound (III) with the compound (V) and the compound (II) may be prepared by a condensation reaction of the compound (IV) with the compound (V).

The condensation reaction may be carried out in an inert organic solvent. Examples of the inert organic solvents are ethanol, n-propanol, toluene, chlorobenzene, chloroform, dimethylformamide, N-methylpyrrolidone, dimethylsulfoxide, sulfolane, acetonitrile, acetic anhydride and mixtures thereof.

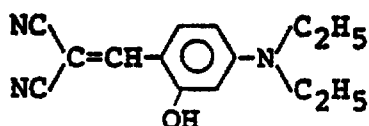
The compound (III) is mixed with the compound (IV) in the inert organic solvent. Then, a catalyst is added to the mixture. The catalyst is preferably an organic base such as, piperidine, pyridine, triethylamine and a mixture of piperidine and glacial acetic acid. The reaction mixture is kept at a temperature of from 0 to 100°C, preferably from 20 to 80°C, for 0.5 to 20 hours, preferably for 1 to 10 hours to proceed the condensation reaction. Then, the solvent is removed from the reaction mixture to leave a crude cake of the compound of the formula (I) or (II). The crude cake can be purified by a conventional method, for example, recrystallization from an adequate solvent such as those used in the condensation reaction. When the compound (I) or (II) contains the hydroxyl group as the substituent in R¹ or R² or when R³ is the hydroxyl group, the hydroxyl group can be derived through hydrolysis of a corresponding hydrolyzable group.

The compound of the formula (I) or (II) 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.

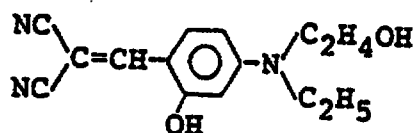
Also, a photoresist which comprises a cresol novolak resin and an ester of polyhydroxybenzophenone with naphthoquinone-1,2-diazide sulfonic acid is preferably used. The cresol novolak resin can be prepared by a reaction of meta-cresol and/or para-cresol with formalin, or a reaction of meta-cresol, para-cresol and 3,5-xenol 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.

Among the compounds of the formula (I) or (II), those having absorption in a wavelength range not longer than 550 nm, particularly between 350 to 400 nm are preferably used in the photoresist composition.

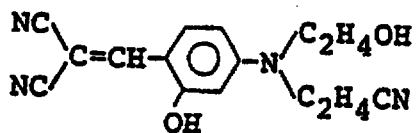
Preferred examples of the compounds (I) which are suitable as the light absorber in the photoresist composition according to the present invention are as follows. These examples will not limit the scope of the present invention.



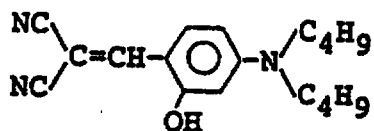
(1)



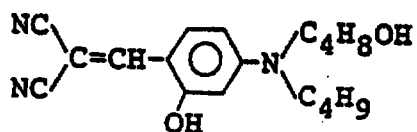
(2)



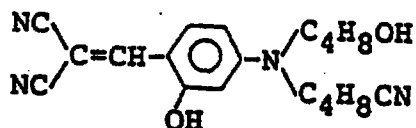
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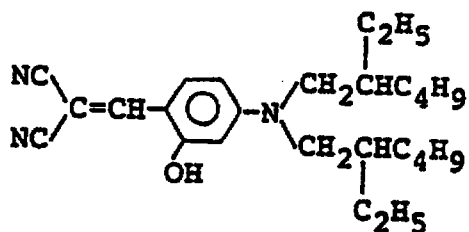
(4)



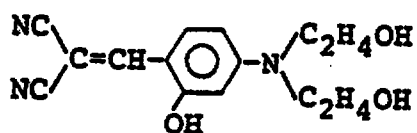
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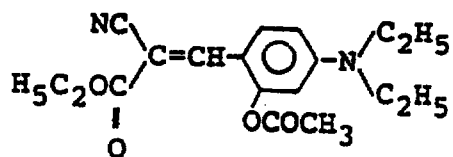
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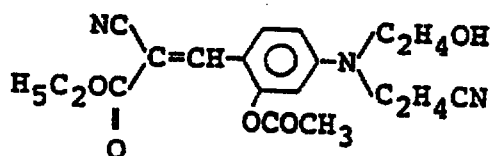
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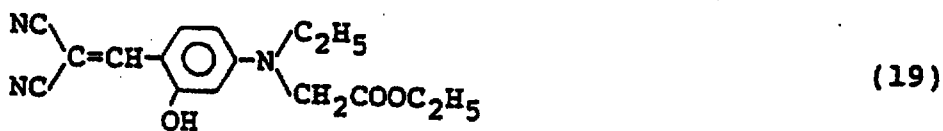
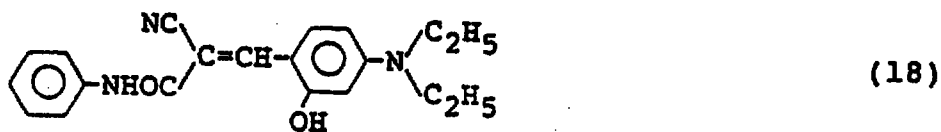
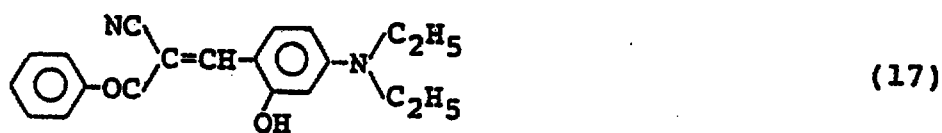
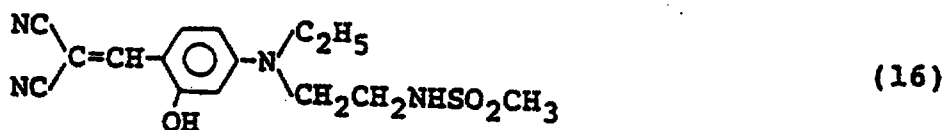
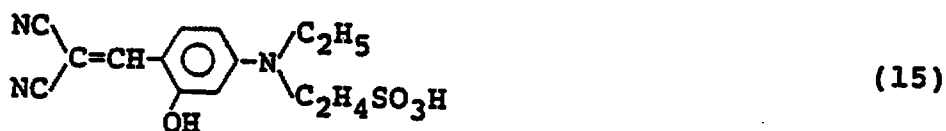
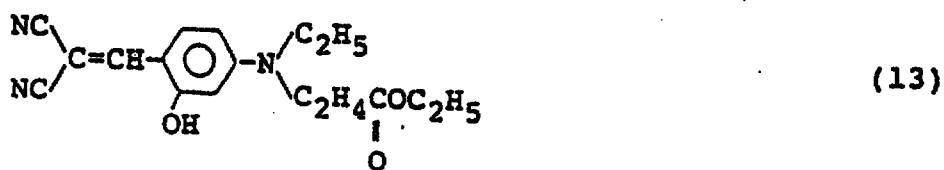
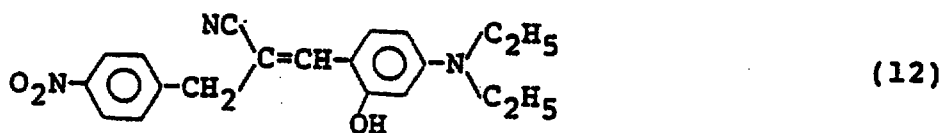
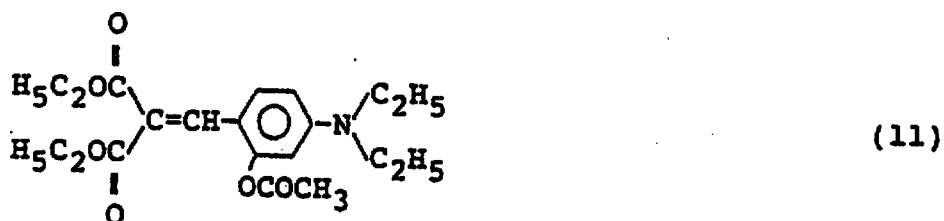
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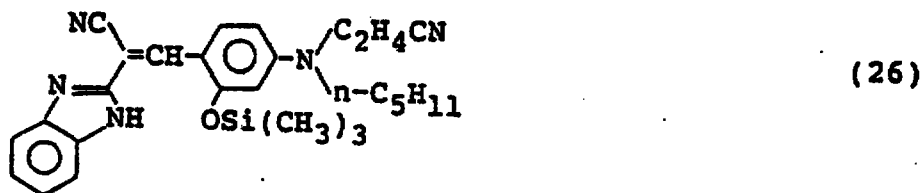
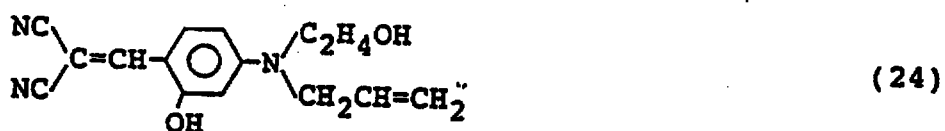
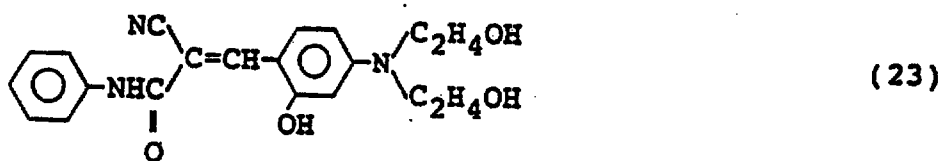
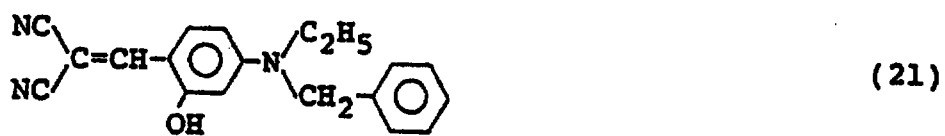
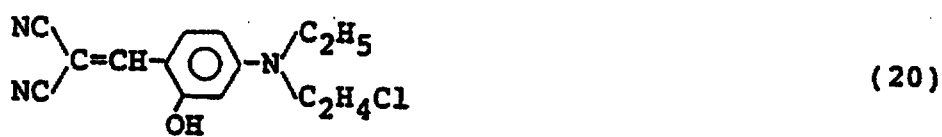


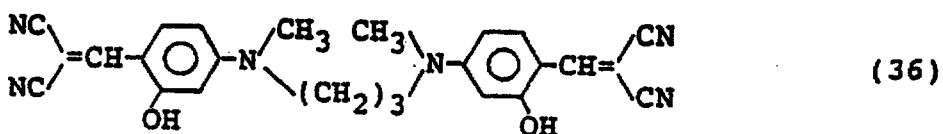
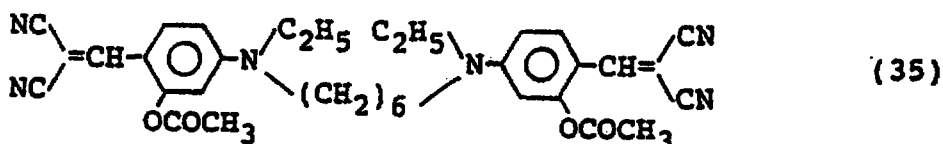
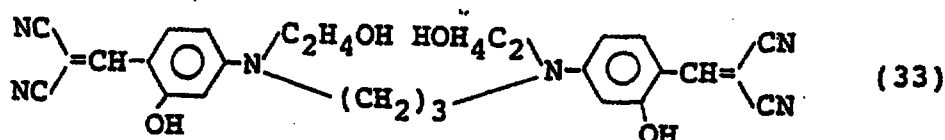
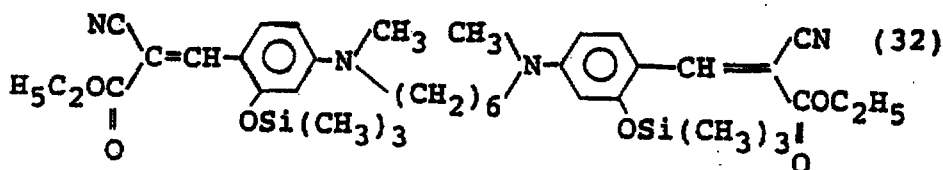
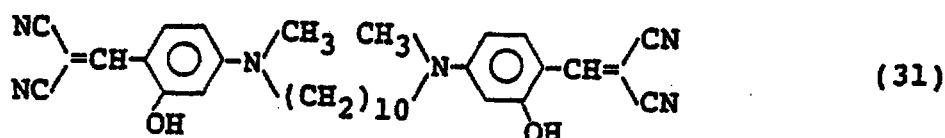
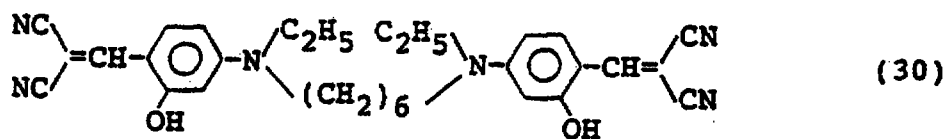
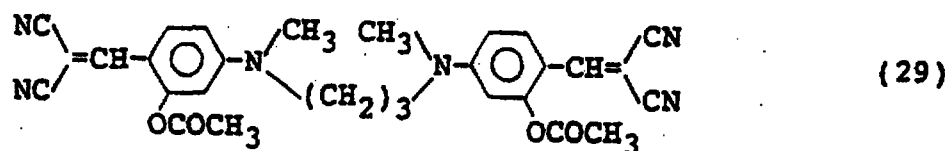
(9)



(10)







The amount of the compound (I) to be added to the photoresist composition is from 0.1 to 20 % by weight, preferably from 0.2 to 10 % by weight based on the weight of the solid component in the photoresist.

The amount of the compound (II) to be added to the photoresist composition is from 0.1 to 15 % by weight, preferably from 0.1 to 8 % based on the weight of the solid component in the photoresist.

If the amount of the compound (I) or (II) is smaller than the above lower limit, the photoresist composition cannot prevent the halation sufficiently. If the amount of the compound (I) or (II) 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 light absorber.

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.

In addition to the light absorber in the photoresist composition, the compounds (I) and (II) can be used as coloring materials in dyeing, sublimation thermal transfer printing, or color filters.

The styryl compounds of the formulae (I) and (II) are easily dissolved in organic solvents such as xylene, ethyl cellosolve, cyclohexanone, cellosolve acetate and butyl acetate. These styryl compounds has 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 compounds (I) or (II) 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.

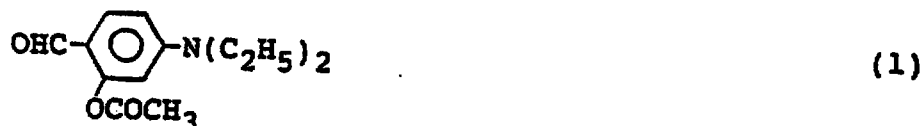
Since styryl compounds of the present invention do not precipitate even after long storage, an uneven coating due to the precipitation can be prevented.

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.

Example 1

2.36 Grams of a compound of the formula:



was mixed with 0.79 g of a compound of the formula:



in 20 ml of ethanol followed by stirring for 6 hours at 22-25°C.

Then ethanol was distilled off from the mixture to obtain a crude cake, which was recrystallised from ethanol to obtain a purified cake (2.12 g) of the compound of the formula:



Melting point: 106-107°C

Absorbance of the compound (3) in ethyl cellosolve acetate:

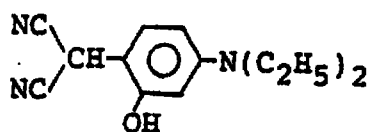
λ_{max} : 436 nm

ϵ : 6.53×10^4

Example 2

To a mixture of 2.00 g of the compound (3) obtained in Example 1 and 70 ml of ethanol, 6 ml of conc. HCl aq was added and stirred for 2 hours at 55-60°C. After cooling down to 20-22°C, the resulting precipitate was filtered off to obtain 1.35 g of a crude cake. The crude cake was recrystallized from ethanol

to obtain a purified cake (1.35 g) of the compound of the formula (4):



(4)

10 Melting point: 235-236 °C

Absorbance of the compound (4) in ethyl cellosolve acetate:

$\lambda_{\max}$: 421 nm

ϵ : 5.01×10^4

15 Examples 3-12

In a similar manner to that described in Examples 1 and 2, compounds shown in Table 1 were prepared.

Table 1

Ex. No.	Chemical structure	Maximum absorbing wavelength (nm) in ethyl cellosolve acetate
3		439
4		398
5		424
6		423
7		415
8		433
9		435
10		419
11		420
12		430

Examples 13 and 14 and Comparative Examples 1 and 2

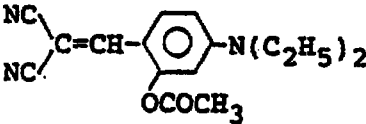
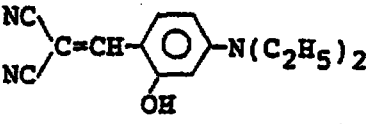
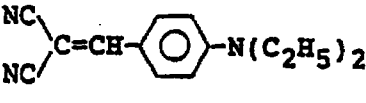
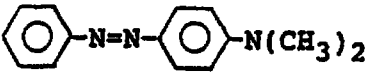
Photoresist compositions were prepared by adding each dye compound shown in Table 2 to a positive photoresist PF-6200 (manufactured by Sumitomo Chemical Company, Limited; a solid content of 31.0 % by weight), which comprises a novolak resin (Mw = 12,000) prepared mainly from m-cresol and at least one

compound having o-quinone diazide groups. The amount of each dye compound added was 0.68 % by weight based on the solid amount in the positive photoresist.

Each of the photoresist compositions was coated on a 4 inch square 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. Subsequently, the silicon wafer was baked for 1 minute on a hot plate kept at 100°C, 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 summarized in Table 2.

In Comparative Examples 1 and 2, dyes disclosed in Japanese Patent Kokai Publication Nos. 93445/1986 and 37562/1976 were used, respectively.

Table 2

Example No.	Chemical structure	Relative sensitivity	Absorbance ratio
Example 13		0.5-0.6	1.0
Example 14		0.5-0.6	0.76
Comparative Example 1		1.0	0.95
Comparative Example 2		1.9	0.75

As understood from the results in Table 2, 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 antishrinkage.

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.

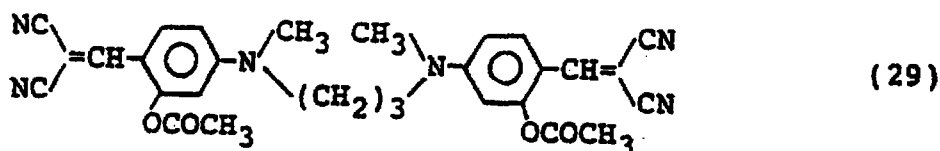
Inspection on deposits remained between patterns revealed that no precipitation was found.

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 15

A pattern was formed on an aluminum wafer by the same procedures as in Examples 13-14 except that the compound of the formula:



was used in place of the compounds shown in Table 2. The pattern with high sensitivity was formed.

The pattern could be resolved sharply and no notching caused with the reflected light on the side surface of the patterns was found.

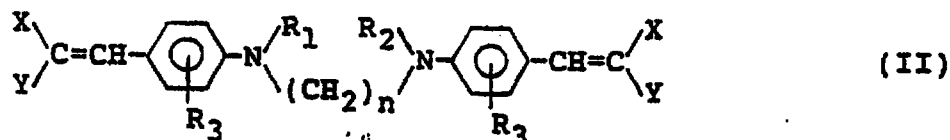
The photoresist composition in this Example is also excellent in antisublimation. Inspection on deposits remained between the patterns revealed that no precipitation was found.

Claims

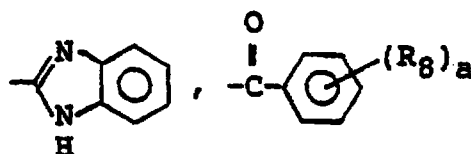
1. A styryl compound of the general formula:



or



wherein R_1 and R_2 are the same or different and a hydrogen atom, an optionally substituted alkyl group, an optionally substituted alkenyl group or an optionally substituted aralkyl group or R_1 and R_2 may form a ring together with the nitrogen atom to which they are bonded, which ring may include at least one hetero atom in addition to said nitrogen atom; R_3 is $-\text{OH}$, $-\text{OCOR}_4$ or $\text{OSi}(\text{R}_5)_3$; X and Y are the same or different and are $-\text{CN}$, $-\text{COOR}_4$, $-\text{CONR}_6\text{R}_7$,



or

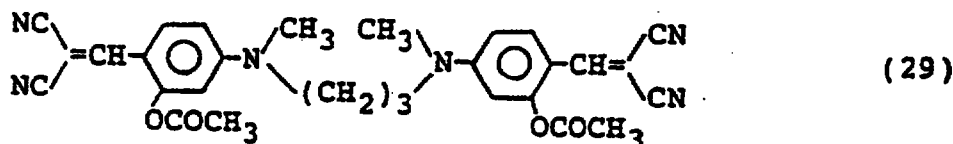


R_4 and R_5 are each an alkyl group; R_6 , R_7 , R_8 and R_9 are the same or different and a hydrogen atom,



Example 15

A pattern was formed on an aluminum wafer by the same procedures as in Examples 13-14 except that the compound of the formula:



was used in place of the compounds shown in Table 2. The pattern with high sensitivity was formed.

The pattern could be resolved sharply and no notching caused with the reflected light on the side surface of the patterns was found.

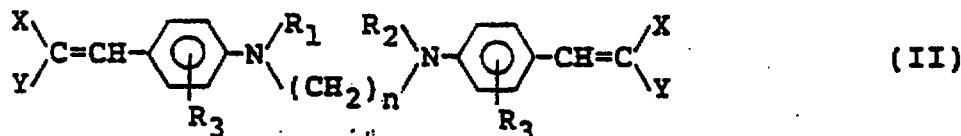
The photoresist composition in this Example is also excellent in antiscumulation. Inspection on deposits remained between the patterns revealed that no precipitation was found.

Claims

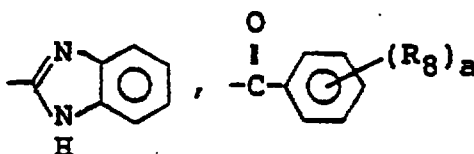
1. A styryl compound of the general formula:



or



wherein R_1 and R_2 are the same or different and a hydrogen atom, an optionally substituted alkyl group, an optionally substituted alkenyl group or an optionally substituted aralkyl group or R_1 and R_2 may form a ring together with the nitrogen atom to which they are bonded, which ring may include at least one hetero atom in addition to said nitrogen atom; R_3 is $-\text{OH}$, $-\text{OCOR}_5$ or $\text{OSi}(\text{R}_5)_3$; X and Y are the same or different and are $-\text{CN}$, $-\text{COOR}_4$, $-\text{CONR}_6\text{R}_7$,



or



R_4 and R_5 are each an alkyl group; R_6 , R_7 , R_8 and R_9 are the same or different and a hydrogen atom.

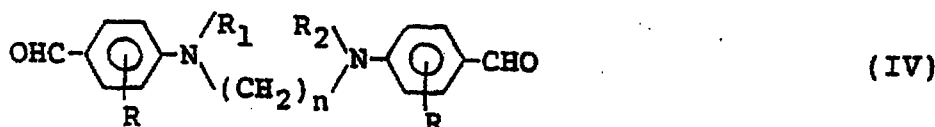


an optionally substituted lower alkyl or phenyl group; n is a number of 2 to 15; and a and b are the same or different and a number of 1 to 2.

2. A process for preparing a styryl compound of the general formula (I) or (II) as claimed in claim 1, which comprises reacting a compound of the general formula:



or



wherein R_1 , R_2 and n are same as defined in claim 1 and R is $-\text{OCOR}_5$ or $-\text{OSi}(\text{R}_5)_3$ with a compound of the general formula:



wherein X and Y are same as defined in claim 1.

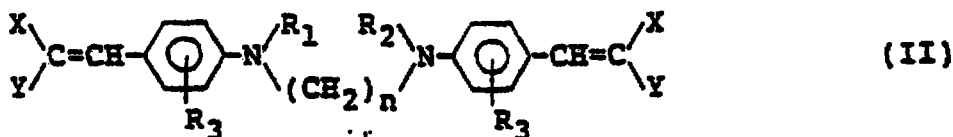
3. A photoresist composition which comprises the compound of the general formula (I) or (II) as claimed in claim 1.

Patentansprüche

1. Styryl-Verbindung der allgemeinen Formel:



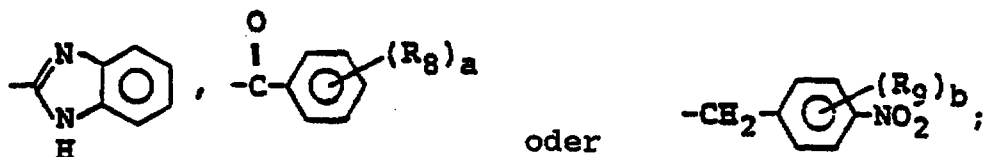
oder



wobei R_1 und R_2 gleich oder verschieden sind und ein Wasserstoffatom, einen gegebenenfalls substituierten Alkylrest, einen gegebenenfalls substituierten Alkenylrest oder einen gegebenenfalls substituierten Aralkylrest bedeuten oder R_1 und R_2 zusammen mit dem Stickstoffatom, an das sie gebunden sind, einen Ring bilden, wobei der Ring mindestens ein Heteroatom zusätzlich zu dem Stickstoffatom umfassen kann; R_3 eine $-\text{OH}$ -Gruppe, einen $-\text{OCOR}_5$ - oder $-\text{OSi}(\text{R}_5)_3$ -Rest darstellt; X



und Y gleich oder verschieden sind und die Reste $-\text{CN}$, $-\text{COOR}_4$, $-\text{CONR}_6\text{R}_7$

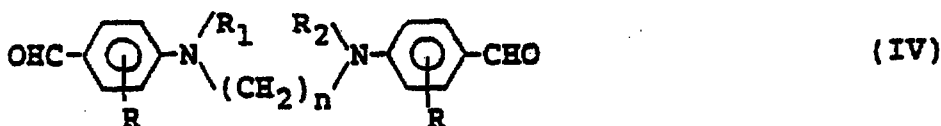


10 bedeuten; R_4 und R_5 jeweils einen Alkylrest darstellen; R_6 , R_7 , R_8 und R_9 gleich oder verschieden sind und ein Wasserstoffatom, einen gegebenenfalls substituierten Niederalkylrest oder eine Phenylgruppe bedeuten; n eine Zahl im Wert von 2 bis 15 ist; und a und b gleich oder verschieden sind und die Zahl 1 oder 2 bedeuten.

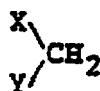
- 15 2. Verfahren zur Herstellung einer Styrylverbindung der allgemeinen Formel (I) oder (II) nach Anspruch 1, umfassend die Umsetzung einer Verbindung der allgemeinen Formel:



25 oder



35 wobei R_1 , R_2 und n die in Anspruch 1 angegebene Bedeutung haben und R einen $-\text{OCOR}_5$ - oder $-\text{OSi}(\text{R}_5)_3$ -Rest bedeutet, mit einer Verbindung der allgemeinen Formel



45 in der X und Y die in Anspruch 1 angegebene Bedeutung haben.

- 50 3. Photoresist-Zusammensetzung, umfassend die Verbindung der allgemeinen Formel (I) oder (II) nach Anspruch 1.

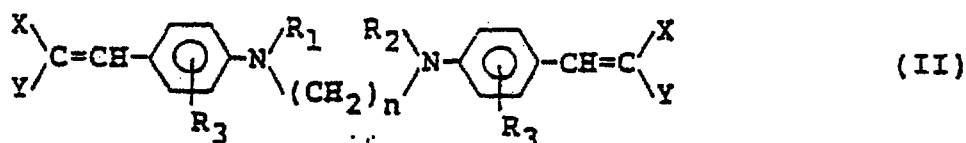
Revendications

- 55 1. Composé de styryle de formule générale :

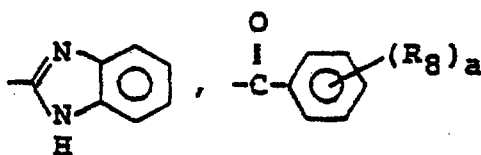




ou



dans laquelle R₁ et R₂ sont identiques ou différents et représentent chacun un atome d'hydrogène, un groupe alkyle facultativement substitué, un groupe alcényle facultativement substitué ou un groupe aralkyle facultativement substitué, ou bien R₁ et R₂ pris ensemble avec l'atome d'azote auquel ils sont liés peuvent former un cycle qui peut contenir au moins un hétéroatome en plus dudit atome d'azote; R₃ est -OH, -OCOR₅ ou -OSi(R₅)₃; X et Y sont identiques ou différents et représentent chacun -CN, -COOR₄, -CONR₆R₇,



ou

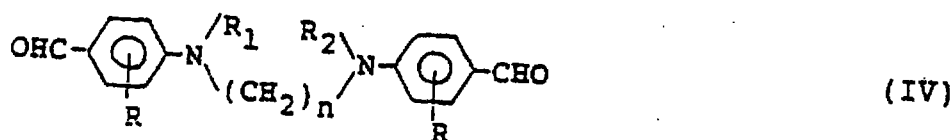


R₄ et R₅ sont chacun un groupe alkyle; R₆, R₇, R₈ et R₉ sont identiques ou différents et représentent chacun un atome d'hydrogène, un groupe alkyle inférieur facultativement substitué ou un groupe phényle; n est un nombre de 2 à 15; et a et b sont identiques ou différents et chacun égal à 1 ou 2.

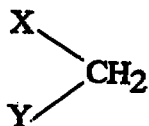
2. Procédé pour préparer un composé de styryle de formule générale (I) ou (II) selon la revendication 1, qui comprend la réaction d'un composé de formule générale



ou



dans laquelle R₁, R₂ et n sont définis comme à la revendication 1 et R est -OCOR₅ ou -OSi(R₅)₃ avec un composé de formule générale



(v)

dans laquelle X et Y sont définis comme à la revendication 1.

3. Une composition pbtorésistante qui comprend le composé de formule générale (I) ou (II) selon la revendication 1.