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 C4D3X

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(54) POSITIVE QUINONE DIAZIDE PHOTORESISTS

(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation organised and existing under the laws of the State of New York, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates generally to additives to positive quinone diazide photoresists. The invention has particular application in, but is not limited to, the generation of microminiature circuit patterns by electron beam or light exposure of positive photoresists.

A positive photoresist is an organic material which, when exposed to radiation, undergoes chemical reactions which result in solubilizing the exposed areas. Until recently these reactions had to be initiated by light rather than electrons. However, Haller et al (IBM Journal, May 1968, pp. 251—256) reported successful results exposing cellulose acetate and polymethyl methacrylate to electron beams. Because it is possible to generate electron beams of substantial energy but of only 0.1 μ or smaller diameter, their use in the generation of extremely small circuit patterns may be preferred to the use of light. Electron beams also have a much better resolution capability than is possible when using an optical mask and light exposure, and they have a much greater depth of focus. For these reasons, it is often highly desirable to expose positive photoresists with electron beams. This also applies to negative photoresists, of course, and they are also amenable to electron bombardment. Where exposure with light is preferred, a more sensitive photoresist will, of course, reduce exposure times. In order that the preferred embodiment of the invention will be more fully understood, some attention is necessary to the procedures for generating microminiature circuit patterns.

The procedures for generating a microminiature circuit pattern by either electron bombardment or light exposure of a positive photoresist are well established, and are summarized briefly below. The substrate is typically an oxidized silicon wafer or a chromium coated glass plate. The photoresist is applied to the substrate, which may then be spun at high speed to leave an even film of the photoresist, having a controlled thickness, on the substrate surface. Alternatively, the photoresist may be sprayed on. The photoresist-coated substrate is then cured to form an insoluble coating and dried or baked briefly to improve adhesion. The coated substrate is then placed in a vacuum chamber and, when the vacuum has been established, the substrate is exposed or subjected to light exposure or electron bombardment in the desired pattern and with an appropriate dosage. The substrate is then placed in a developer, which is a solvent for the soluble (i.e. exposed) portion of the resist, to dissolve and remove the exposed portions. It is again dried or baked. The desired pattern area on the substrate is now free of any covering film, and etching, plating or oxidizing follows. After this step, the remaining resist is stripped off.

There are a variety of limitations imposed upon the radiation step, which will be summarized here.

Briefly, the amount of radiation must fully expose the photoresist all the way down to the substrate, or else the underlying, insoluble photoresist will not be dissolved in the developer. On the other hand, too much radiation causes a loss of resolution

and, ultimately, insolubilization. The amount of radiation necessary to solubilize a photoresist is apparently a function of the molecular weight of the material, and the gross amount of radiation.

The efficiency of the solubilizing reactions induced by an electron beam is related to the accelerating potential of the electrons, penetration range (also a function of potential) and other factors. For instance, it has been determined that the maximum film thickness that can be exposed by 5 KV electrons is about 6500 Å and by 10 KV electrons is about 2 μ. On the other hand, photoresists should initially be at least 6000 Å thick to avoid pinhole problems. Other limitations which must be considered are electron scatter within the film and backscatter from the substrate, though these are of a lesser order.

The efficiency of light-induced solubilization reactions is related to the wavelength of the light and the absorption properties of the photoresist.

While a great deal of work has been done in increasing the sensitivity of negative photoresists to light, the above-noted Haller et al. reference is one of the few later literature references specifically directed to the electron beam exposure of positive photoresists. Prior workers in the field of photolithography, where photoresists were first employed, have proposed a large number of compounds as positive photoresists. This work is not readily summarized, but the following references describe the quinone diazide photoresists useful in the present invention. In Canadian patent No. 747,047 assigned to the Shipley Co., these photoresists are designated as naphthoquinone-(1,2) diazide sulphonic acid esters. The following United States patents, all assigned to the Azoplate Corporation described various formulations of the same kind of positive photoresists. United States Patent No. 3,046,111 teaches using several diazide residues by reacting an aminohydroxy compound with the sulphonic acid or its chloride. United States Patent No. 3,046,112 defines some of the basic formulae for orthoquinone diazide sulphones. Many variations are proposed, and additions of resins, dyestuffs and other additives are discussed. In United States Patent No. 3,046,115 the addition of an auxochromous group, is said to intensify colouring. In United States Patent No. 3,046,118, it is preferred to have two of the sulphonic acid residues linked in the manner of an ester, so as to reduce the heating required. In United States Patent No. 3,148,983, a certain basic formula is proposed. Lastly, in United States Patent No. 3,184,310 the inclusion of at least one free hydroxyl group is said to be beneficial, and another general formula is proposed.

As used herein, the expression "quinone diazide photoresist" is intended to refer generically to all of the foregoing types of compounds.

In accordance with the present invention there is provided a process of generating a pattern on a substrate by exposure to an electron beam or light and developing, wherein the substrate is coated with a positive quinone diazide photoresist containing at least 0.5 weight percent of a compound which increases the sensitivity of the photoresist to exposure, the sensitivity increasing compound being selected from:—

(a) aromatic compounds containing at least two heterocyclic nitrogen atoms having bonds to atoms selected from nitrogen atoms, carbon atoms and hydrogen atoms, at least one of said heterocyclic nitrogen atoms being bonded to a hydrogen atom, said ring containing no other heterocyclic atoms;

- (b) 2-azacyclononanone;
- (c) indole;
- (d) quinazoline; and
- (e) 6,7-dihydro-5H-pyrrolo[3,2-d]tetrazole.

The embodiments of the present invention provide new and improved additives to quinone diazide photoresists which increase the sensitivity thereof to electrons and to light. The additives result in increased reactivity of the photoresist itself.

The radiation is reduced and, hence, the exposure time required to fully expose specific, positive photoresists, is reduced by incorporating the novel additives therein.

For a better understanding of the invention, reference is made to the accompanying drawing, in which:—

FIGS. 1—2 are plots of resist thickness vs. electron flux density for exposure of 6000 Å films of Shipley 1350 positive resist and Shipley 1350 plus certain additives of embodiments of the invention; and

FIG. 3 is a plot of resist thickness vs. exposure time to light for exposure of 6000 Å films of Shipley AZ-1350 both alone and with an additive of an embodiment.

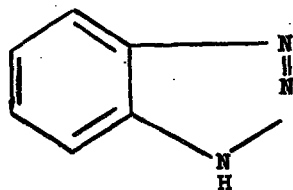
In the embodiments small amounts of aromatic and certain other compounds described below are added to positive photoresists of the quinone diazide type. It is

not known why these compounds enhance the sensitivity of these particular resists, and no explanation is offered. That they do provide significantly better results is manifest from the examples set forth below. One group of operative compounds are triazoles, and while other workers have established that certain benzotriazole compounds absorb ultraviolet light, this does not fully explain their apparent sensitivity to electron beams or to light (see, in this regard United States Patent No. 3,262,943 assigned to E. I. du Pont de Nemours and Co.).

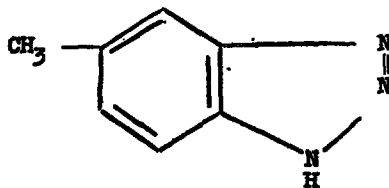
It is not known that in film form, quinone diazide photoresists form true polymers or form a high molecular weight compound. However, it is believed that, under the influence of actinic radiation, the oxygen forms a COOH group which is soluble in bases. As sold commercially, however, the photoresists are believed to contain other reactive groups, of a type unknown, as catalyzers and sensitizers. Compatible solvents are used if necessary, for viscosity control. These positive photoresists utilized in connection with the present invention are sold by various companies, including the Shipley Company under such tradenames as Shipley AZ-1350 and AZ-1350H, and Eastman Kodak Company as KAR-3.

Most of the compounds which have been found operative to increase the sensitivity of quinone diazide photoresists are compounds of an aromatic character that contain two or more heterocyclic nitrogen atoms, at least one of which is bonded to a hydrogen atom. Further, the ring can contain no other heterocyclic atoms, and the nitrogen atoms cannot be bonded to atoms other than nitrogen, carbon or hydrogen atoms. Any compound meeting this definition will increase the sensitivity of a quinone diazide resist. These compounds also increase the amount of radiation required to over-expose (i.e., insolubilize) the photoresist of which the following are examples:

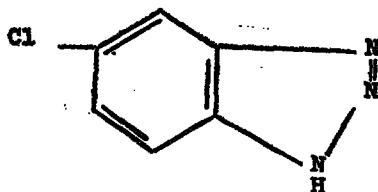
benzotriazole



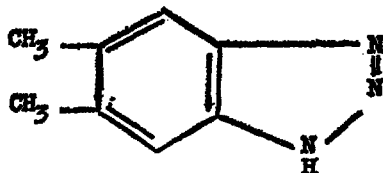
5-methylbenzotriazole



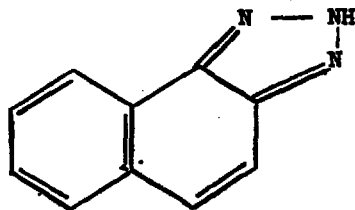
5-chlorobenzotriazole



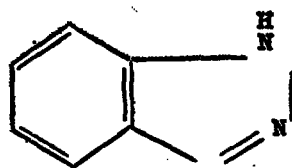
5,6-dimethylbenzotriazole



1,2-naphthotriazole



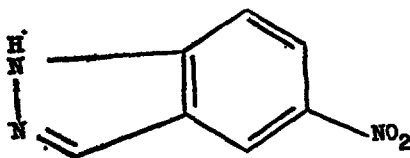
indazole



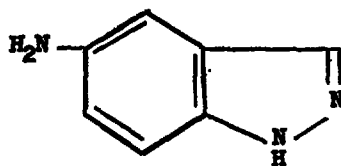
5

5-nitroindazole

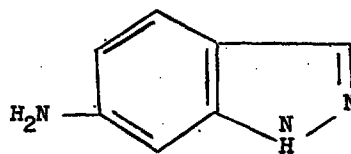
5



5-aminoindazole



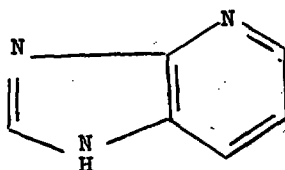
6-aminoindazole



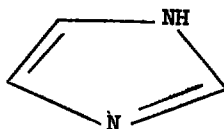
10

4-azabenzimidazole

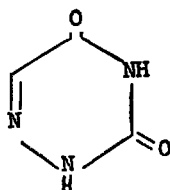
10



imidazole

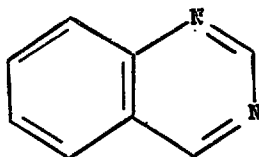


6-azauracil

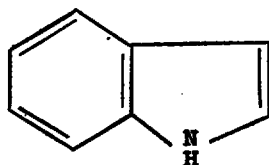


Compounds which have been found to be effective but which do not fit the above general definition are as follows:

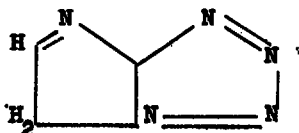
quinazoline



indole

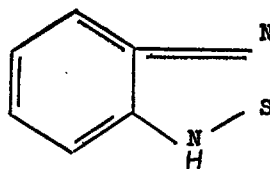


6,7-dihydro-5H-pyrrolo[3,2-d]tetrazole

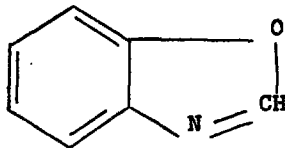


In contrast to the foregoing, the following compounds were found to be ineffective in increasing the sensitivity of these photoresists:

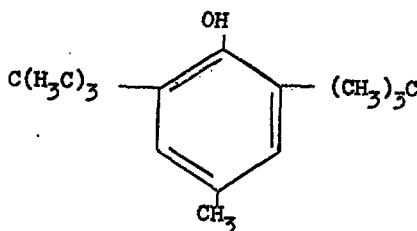
benzothiadiazole



benzoxazole



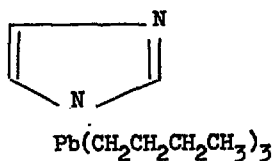
di-t-butyl-p-cresol



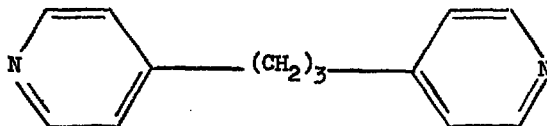
5

1-(tri n-butylplumbi)imidazole

5



4,4'-trimethylenedipyridine



octadecylamine

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Solubility of the effective compounds of the embodiments in resists of the type described in substantial, i.e., well above the normal addition range. There should be at least 0.5 weight per cent of the additive compound employed although the amount is not critical; generally an amount equal to from 0.5 to 3 per cent (by weight) is sufficient. The following specific examples will illustrate the improvement obtained by the additives.

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EXAMPLES

To establish a basis for comparison, tests were first made with Shipley AZ-1350 without any additives. The resist was applied to a chromium coated glass plate. This was then spun so that the resulting coating, after baking at 150°C. for 10 minutes, was 6000 Å thick. The coated plate was then placed in a vacuum chamber and radiated with electrons accelerated at 15 KV. The plate was developed by washing with an NaOH solution and deionized water, and baked at 150°C. for 10 minutes. The following results were obtained:

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Electron flux required to give a fully developed spot, $\mu\text{coul}/\text{cm}^2$

Bottle #1 (AZ-1350)
Bottle #2 (AZ-1350)
Bottle #3 (AZ-1350H)
Bottle #4 (AZ-1350)

8
24
16
32

30

30

The following additives in weight per cent. were then tested with the Bottle #1 resist:

		Flux, $\mu\text{coul}/\text{cm}^2$	
5	0.5—1.0% benzotriazole	4	
	3.0% benzotriazole	4	5
	1.0—2.0% 5-methylbenzotriazole	4	

Thus, in each instance, the exposure required to give a fully developed spot was reduced by at least half.

The following additives in weight per cent. were tested with the resist in Bottle #2:

	Flux, $\mu\text{coul}/\text{cm}^2$
1.0% 5-chlorobenzotriazole	8
1.0% 5,6-dimethylbenzotriazole	8
1.0% 1,2-naphthotriazole	8

These three additives each reduced the exposure required to achieve a fully developed spot by a factor of three.

Lastly, the addition of 1.0% by weight 5-methylbenzotriazole to the resist of Bottle #3 reduced the exposure required to achieve a fully developed spot from 16 to 8 $\mu\text{coul}/\text{cm}^2$.

The very substantial differences in sensitivity from one bottle to another were found to be a function of shelf life. In general, the older the photoresist, the greater the electron flux needed to give a fully developed spot. This is shown graphically in FIG. 1. With a positive resist solubilizing reactions take place upon exposure, so the resist is completely exposed when, after development, there is none left. If the resist is overexposed, however, crosslinking reactions will be brought about, and the film will be insolubilized. In FIG. 1, Curve A is for a newly purchased bottle of AZ-1350, Curve B is for a bottle of the same material, but two weeks older, and Curve C is for a three month old bottle of the same material (the two latter bottles were kept refrigerated). Curve D is for the cross-linking (overexposure) reactions, which are not effected by aging. Some of the additives may also lose their effectiveness after storage for a period of time.

FIG. 2 illustrates the effect of adding 1% by weight benzotriazole to the resist. Again Curve A is for newly purchased AZ-1350, but Curve C is for resist from a four-month older bottle. It is significant to note that the additive not only reduces the flux required for full exposure, but also increases the amount of flux that is needed before crosslinking commences, as can be seen by comparing Curves A¹ and C¹ with Curve D of FIG. 1. Thus, the addition of triazole compounds widens the "window" which results in full exposure.

The following tests report results of other additives of the invention, including flux required to just solubilize a full spot and flux just causing insolubilizing, using bottle #4, the initial values being 32 and 160 $\mu\text{coul}/\text{cm}^2$, respectively.

	Additive in weight %	Solubilizing Flux, $\mu\text{coul}/\text{cm}^2$	Insolubilizing Flux, $\mu\text{coul}/\text{cm}^2$	
45	1.8% indazole	16	160	
	1.3% 5-nitroindazole	8	160	45
	1.4% 5-aminoindazole	8	160	
	1.12% 6-aminoindazole	24	160	
	1.27% 6,7-dihydro-5H pyrrolo[3,2-d] tetrazole	4	160	
50	1.05% 4-azabenzimidazole	16	160	50
	1.13% imidazole	8	560	
	1.53% quinazoline	8	640	
	1% 6-azauracil	16	320	
	1.2% 2-azacyclononan-one	16	900	
55	1.25% indole	24	560	55

The additives of the embodiments also increase the sensitivity of the resist to light. Referring to FIG. 3, it was found that the time needed for complete exposure of a 6000 Å film of AZ-1350 by a filtered (+3100 Å) 150 watt xenon lamp was three minutes, as shown in Curve E. Two weight per cent. of benzotriazole was added

to AZ-1350 which was one week older than the material used to generate Curve E, and exposure of the photoresist with the additive is plotted as Curve F. As can be seen, complete exposure time with the additive was reduced to two minutes, even with older material. Similar results have been observed for other additives of the

WHAT WE CLAIM IS:—

1. A process of generating a pattern on a substrate by exposure to an electron beam or light and developing, wherein the substrate is coated with a positive quinone diazide photoresist containing at least 0.5 weight per cent. of a compound which increases the sensitivity of the photoresist to exposure, the sensitivity increasing compound being selected from:—

permissible
(a) aromatic compounds containing at least two heterocyclic nitrogen atoms having bonds to atoms selected from nitrogen atoms, carbon atoms and hydrogen atoms, at least one of said heterocyclic nitrogen atoms being bonded to a hydrogen atom, said ring containing no other heterocyclic atoms;

(b) 2-azacyclononane;

(c) indole;

(d) quinazoline; and

(e) 6,7-dihydro-5H-pyrrolo[3,2-d]tetrazole.

2. A process according to claim 1, wherein the said compound is added in amounts such that its concentration in the photoresist is within the range of from 0.5 to 3 weight per cent.

3. A process according to claim 1 or 2, wherein the said aromatic compounds are selected from benzotriazole; 5-methylbenzotriazole; 5-chlorobenzotriazole; 5,6-dimethylbenzotriazole; 1,2 - naphthotriazole; indazole; 5 - nitroindazole; 5 - aminoindazole; 6-aminoindazole and 4-azabenzimidazole.

4. A system according to claim 1 or 2, wherein the aromatic compounds are selected from imidazole and 6-azauracil.

5. A process of generating a pattern on a substrate, according to claim 1, and substantially as hereinbefore described with reference to any one of the examples.

6. A process of generating a pattern on a substrate, according to claim 1, and substantially as hereinbefore described with reference to any one of the figures of the accompanying drawing.

7. A substrate bearing a pattern generated by the process according to any one of the preceding claims.

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(a) aromatic compounds containing at least two heterocyclic nitrogen atoms having bonds to atoms selected from nitrogen atoms, carbon atoms and hydrogen atoms, at least one of said heterocyclic nitrogen atoms being bonded to a hydrogen atom, said ring containing no other heterocyclic atoms;

(b) 2-azacyclononanone;

(c) indole;

(d) quinazoline; and

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2. A process according to claim 1, wherein the said compound is added in amounts such that its concentration in the photoresist is within the range of from 0.5 to 3 weight per cent.

3. A process according to claim 1 or 2, wherein the said aromatic compounds are selected from benzotriazole; 5-methylbenzotriazole; 5-chlorobenzotriazole; 5,6-dimethylbenzotriazole; 1,2 - naphthotriazole; indazole; 5 - nitroindazole; 5 - aminoindazole; 6-aminoindazole and 4-azabenzimidazole.

4. A system according to claim 1 or 2, wherein the aromatic compounds are selected from imidazole and 6-azauracil.

5. A process of generating a pattern on a substrate, according to claim 1, and substantially as hereinbefore described with reference to any one of the examples.

6. A process of generating a pattern on a substrate, according to claim 1, and substantially as hereinbefore described with reference to any one of the figures of the accompanying drawing.

7. A substrate bearing a pattern generated by the process according to any one of the preceding claims.

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