

PATENT SPECIFICATION

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 C4D3X

(72) Inventor BARRET BROYDE

(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 organized 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 particularly 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 0.1μ 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 a 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 photo-

resist 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 2μ. 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 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 resistivity of the photoresist to overexposure, the overexposure resistivity increasing compound being selected from: 3,4-dinitroaniline, 3,4-dichloroaniline, 3,4-dimethylaniline, 2,3-dimethylquinoxalines, 5-nitro-indoline, 1,3-di-(4-piperidyl)propane, and 5-nitroindole.

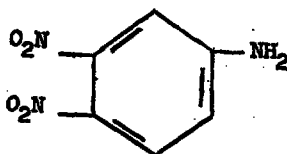
In the embodiments, the additives allow greater exposure time without overexposing (i.e., insolubilizing) the positive photoresist.

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 AZ1350H, and Eastman Kodak Company as KAR-3.

The following compounds have been found to improve the resistance of a photoresist of the quinone diazide type to overexposure:—

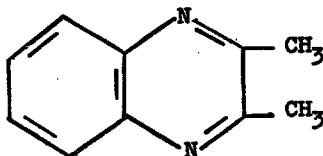
Example 1

3,4-dinitroaniline



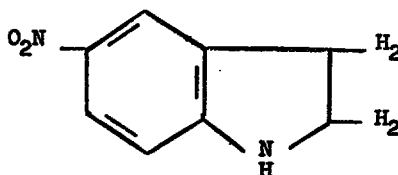
2,3-dimethylquinoxaline

Example 2



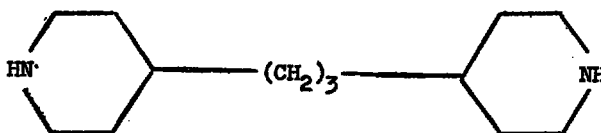
5-nitroindoline

Example 3



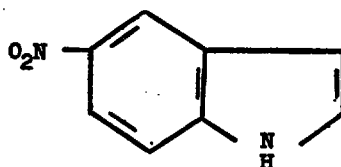
1,3-di-(4-piperidyl) propane

Example 4



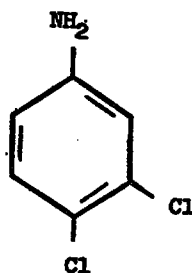
5-nitroindole

Example 5



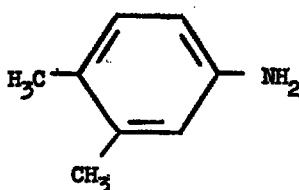
3,4-dichloroaniline

Example 6



3,4-dimethylaniline

Example 7



Solubility of the effective compounds of the embodiments in resists of the type described is 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.

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 tests report results of additives of the invention, including electron flux required to just solubilize a full spot and flux just causing insolubilizing, using Shipley AZ 1350, the initial values being 32 and 160 $\mu\text{coul}/\text{cm}^2$, respectively.

		Solubilizing Flux, $\mu\text{coul}/\text{cm}^2$	Insolubilizing Flux, $\mu\text{coul}/\text{cm}^2$	
15	Additive in weight %			15
	1.85% 3,4-dinitroaniline	40	480	
	1.0% 5-nitroindoline	32	720	
	1.3% 1,3-di-(4-piperidyl) propane	40	400	20
20	1.0% 5-nitroindole	32	400	
	1.85 3,4-dichloroaniline	32	400	
	1.85% 3,4-dimethylaniline	32	720	

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 percent of a compound which increases the resistivity of the photoresist to overexposure, the overexposure resistivity increasing compound being selected from:

3,4-dichloroaniline, 3,4-dimethylaniline, 3,4-dinitroaniline, 2,3-dimethyl-quinoxaline, 5-nitro-indoline, 1,3-di-(4-piperidyl)propane, and 5-nitroindole.

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 percent.

3. A process of generating a pattern on a substrate according to claim 1, substantially as herein before described with references to any one of the Examples.

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

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 - 30 3,4-dichloroaniline, 3,4-dimethylaniline, 3,4-dinitroaniline, 2,3-dimethyl-quinoxaline, 5-nitro-indoline, 1,3-di-(4-piperidyl)propane, and 5-nitroindole.
- 35 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 percent.
3. A process of generating a pattern on a substrate according to claim 1, substantially as herein before described with references to any one of the Examples.
4. A substrate bearing a pattern produced by the process according to any one of the preceding claims.

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