

# PATENT SPECIFICATION

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## DRAWINGS ATTACHED

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## (54) METHODS OF COATING SUBSTRATES WITH PHOTORESISTS

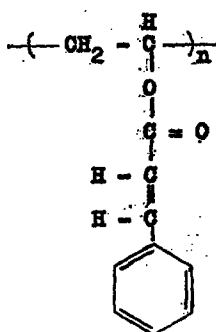
(71) We, WESTERN ELECTRIC COMPANY, INCORPORATED, of 195 Broadway, New York City, New York State, United States of America, a Corporation organized and existing under the laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted 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 to substrates coated with photoresist capable of becoming insoluble upon exposure to electron beam radiation. The invention has particular application in, but is not limited to, the generation of microminiature circuit patterns by electron beam exposure of negative photoresists.

A negative photoresist is an organic material which, when exposed to radiation, undergoes chemical reactions of the type referred to as crosslinking, which reactions result in insolubilizing the exposed photoresist. The crosslinking reactions are of the type that can be initiated either by light or by electrons. Because it is possible to generate electron beams of substantial energy but only  $0.1\mu$  or smaller diameter, their use in the generation of extremely small circuit patterns is 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. The exposure of a conventional positive photoresist involves solubilization of the exposed areas, and the chemical reactions involved are of the scission or degradation type, which also require absorption of light or electrons. Because this type of photoresist requires higher flux densities for proper exposure than negative photoresists require, electron beams are not widely employed in this service. Materials that have been successfully used as electron-sensitive positive photoresists are discussed by Haller et al, *IBM Journal*, May 1968, pp. 251—256.

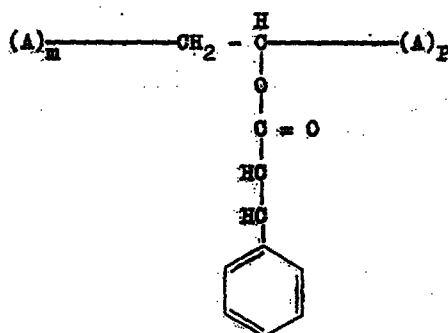
The most common negative photoresists in current use are "Kodak" (Registered Trade Mark) Photoresist ("KPR" Registered Trade Mark) and "Kodak" Thin Film Resist ("KTFR", Registered Trademark). The "KPR" composition is based on the dimerization of vinyl cinnamate, while "KTFR" is based on the crosslinking of polymerized isoprene dimers. Other members of the "KPR" group are "KPR" II and III, and "KOR" (registered trademark for "Kodak" Ortho Resist). Another product "KMER" (registered trademark for "Kodak" Metal Etch Resist) belongs to the "KTFR" group. Examples of the invention will be described with primary reference to use of "KPR" and "KTFR".

The crosslinking and insolubilization of resists is a complex phenomenon, but is believed to be describable, broadly, as follows. A "KPR"-type resist has the following general formula:



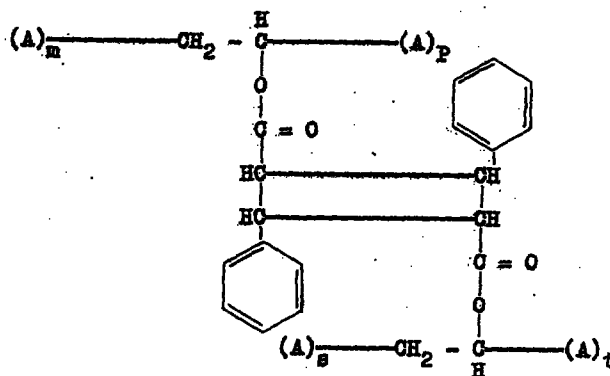
(1)

The number average molecular weight (N.A.M.W.) is 180,000—230,000, and the weight average molecular weight (W.A.M.W.) is 315,000—350,000. Upon exposure to light or electron energy, a diradical is formed:



(2)

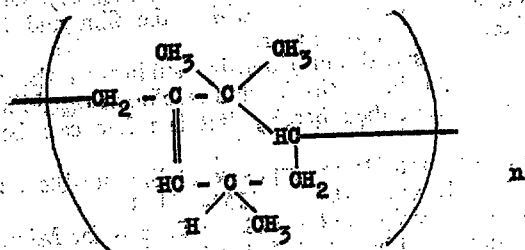
where A is the "KPR" monomer (structure 1 where  $n=1$ ). The diradical then reacts with another diradical to form a 4-member ring:



(3)

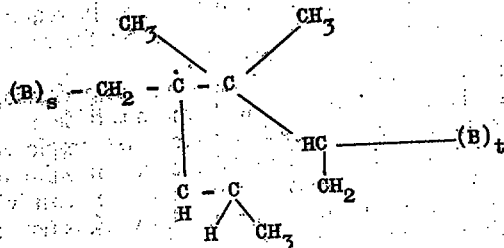
Further excitation and dimerization leads to an insoluble product; no free radicals participate in these reactions.

The "KTFR"-type resists can be characterized as follows:



(4)

These materials have a N.A.M.W. of  $65,000 \pm 5,000$  and a W.A.M.W. of about 100,000, and are insolubilized by free radical reactions. Thus, radiation produces a diradical:



(5)

where B is the monomer of (4). The diradical reacts with other molecules until the free radical terminates. For good resolution, additives are believed to be incorporated to keep the chain short. In all of the above structural formulae, the subscripts (n, m, p, s, t) refer to integers which are determinative of molecular weight. While "KPR" and "KTFR" are insolubilized by different mechanisms, both result in crosslinked systems.

The procedures for generating a microminiature pattern circuit by electron bombardment of a 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 dissolved in a suitable solvent and 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-solvent solution may be sprayed on. In either case, most of the solvent evaporates immediately. The photoresist-coated substrate is then dried or baked briefly to drive off any remaining solvent and to improve adhesion. The coated substrate is then placed in a vacuum chamber and, when the vacuum has been established, it is radiated in the desired pattern and with an appropriate dosage. The coated and radiated substrate is then placed in a developer, which is a solvent for the soluble portion of the resist, to dissolve and remove the unexposed 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 radiating step, but these are fully covered in the prior art (listed below) and need only be summarized here.

Briefly, the amount of radiation must fully expose the photoresist all the way down to the substrate, or else the developed photoresist will float off when the underlying, undeveloped photoresist is dissolved in the developer. On the other hand, too much radiation will cause stripping problems and even polymer degradation. The amount of radiation necessary to form an insoluble photoresist is a function of the molecular weight of the material, and the gross amount of radiation. The efficiency of the crosslinking reactions 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 developed 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 (a 6000 Å film will shrink to about 4000 Å when developed). Other limitations which must be considered are electron scatter within the film and back-scatter from the substrate, though these are of a lesser order.

Prior workers have carried out extensive studies on the foregoing limitations, particularly with respect to the sensitivity and resolution capability of standard resists. This work need not be described herein, but is referenced below for background information:

Thornley et al, "Electron Beam Exposure of Photoresists", J. Electrochem. Soc., Vol. 112, No. 11, Nov. 1965, pp. 1151—1153.

Broers, "Combined Electron and Ion Beam Process for Microelectronics", Microelectronics and Reliability, Vol. 4, 1965, pp. 103—104.

Kanaya et al, "Measurement of Spot Size and Current Density Distribution of Electron Probes by Using Electron Beam Exposure of Kodak Photoresist Films", Zeit. f. Licht-und Elektronioptik, Vol. 25, No. 5, 1967, p. 31.

Matta, "High Resolution Electron Beam Exposure of Photoresists, Electrochemical Technology", Vol. 5, No. 7—8, July—August 1967, pp. 382—385.

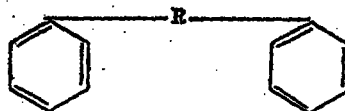
None of these prior workers have made any effort to alter conventional photoresist compositions, although it is significant to note that Thornley et al appreciated the problems which they pose: "For serial exposures, such as may be required in printed circuit generators, the maximum exposure rates are limited by the sensitivities of presently available resists. (Thornley et al, *op cit*, page 1151).

While prior workers who have studied electron beam development of resists to generate small patterns have worked only with the available resists, workers in the field of photolithography, where photoresists were first employed, have proposed literally thousands of compounds as photopolymerization initiators, catalyzers and sensitizers. The end in view was generally to increase the sensitivity or resolution of the photoresist to light of a particular wavelength. This work is not readily summarized, but the following United States patents are considered representative: 2,816,091; 2,831,768; 2,861,057; 3,168,404; 3,178,283; 3,257,664; 3,331,761.

An object of the present invention is to provide improved photoresist compositions.

According to one aspect of the present invention there is provided a method of improving the sensitivity of a photoresist coating to electron radiation comprising coating a substrate with a solvent containing a photoresist composition suitable for the generation of a pattern and a sensitizer therefor, the photoresist composition including either dimers of vinyl cinnamate or a polymerized isoprene and the sensitizer being an organometallic compound having a metallic moiety selected from metals in Groups III, IV or V of the Periodic Table having an atomic number greater than 30 and being present in an amount of up to 5 per cent of the total composition, so that the sensitivity of the photoresist coating to electron radiation is improved.

According to another aspect of the present invention there is provided a method of improving the sensitivity of a photoresist coating to electron radiation comprising coating a substrate with a solvent containing a photoresist composition suitable for the generation of a pattern and a sensitizer therefor, the photoresist composition including either a polyvinyl cinnamate or a polymerized isoprene and the sensitizer being an organic compound having the general formula



wherein R is a radical having one or more carbon atoms and in which a carbon atom adjacent the phenyl ring is bonded to another atom by a double bond and being present in an amount of up to 5 per cent of the total composition, so that the sensitivity of the photoresist coating to electron radiation is improved.

The embodiments of the invention provide additives to standard negative photoresists which result in increased reactivity of the photoresist itself. The sensitivity of a standard negative photoresist is improved by including novel additives therein. The flux density is reduced and, hence, the exposure time required to fully expose a standard photoresist, by incorporating novel additives therein.

Several embodiments of the invention will now be described with reference to the accompanying drawings, in which:—

FIG. 1 is a plot of resist thickness vs. flux density for exposure of 6000 Å films of KPR and KPR plus dibutyl maleate (dashed line), and KPR plus dibutyltin maleate (solid line);

FIG. 2 is a plot similar to FIG. 1 for KTFR (dashed line) and KTFR plus hexaphenyldilead (solid line); and

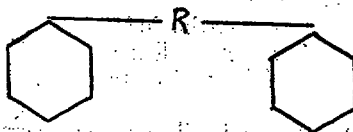
FIGS. 3 to 5 are plots of resist thickness vs. flux density for exposure of 6000 Å films of KTFR (dashed line) and KTFR plus another group of the preferred additives (solid line) of the invention.

The embodiments comprise the addition to a photoresist solvent solution, in small amounts, of additives which increase the sensitivity thereof to electrons.

One group of additives includes solvent-soluble organometallic compounds having a heavy metal moiety selected from Groups III, IV or V of the Periodic Table. As used herein, the term "heavy metal" is defined as a metal having an atomic number greater than 30. These materials result in the increased capture of electrons per unit flux and thus in the increased reactivity, such as crosslinking, of the resist itself.

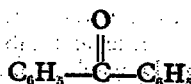
The concentration of the organometallic compound in the solvent-resist solution is below 5% and is generally within the range of about 0.1 to 2% (all percentages used herein are weight percent). Concentrations above 2% will not generally be soluble in the solvent and, if the concentration exceeds the solubility limit, resolution will be lost. In the dried (solvent free) photoresist film, the organometallic concentration will be generally less than 50%.

Another group of additives includes compounds which readily dissociate into free radicals. These enhance the crosslinking of the resists, thus insolubilizing them. There are many compounds which will do this, but most have undesirable side effects, such as causing crosslinking in the dark, without any exposure. Many peroxides and hydroperoxides fall into this category. Compounds having general formula:

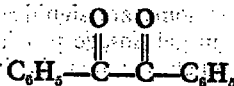


wherein R is a radical having one or more carbons and wherein a carbon adjacent to the phenyl ring is bonded to another atom by a double bond, have proven effective. Three of such compounds are:

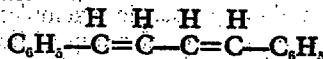
benzophenone



benzil



1,4-diphenyl-1,3-butadiene



The amount of the additive used is important. If too little additive is present, sufficient free radicals will not be generated to cause a maximum effect. On the other hand, if too much of the additive is present, the free radicals will react with each other rather than with the resist, and crosslinking will not be aided. It has been determined that no more than about 5% (all percentages are weight percent) of the additive should be added to the resist-solvent mixture. It should be understood, however, that this may amount to 20% or even 50% of the resist after the solvent is removed. Generally a 1% solution of the additive is preferred.

If one knows the average molecular weight of the photoresist film and the electron accelerating potential, and makes certain assumptions regarding electron penetration, scatter and energy transfer, the gel dose of energy can be calculated from theory (the gel dose is the electron flux necessary to record an image in the film surface, i.e., the

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minimum dose to cause insolubility). Experimental results are in fair agreement with such calculations.

5 Similar calculations, which take into account the presence of a heavy metal ion in the film of the type mentioned above in connection with said organometallic additives show that the gel dose should be lower. This is not entirely unexpected, since heavy metals are noted for their ability to stop or capture electrons (explaining the use of lead as radiation shielding). More precisely, the energy loss when an electron collides with a heavy metal is quite high, and energy transfer sites will overlap when a metal is present in the film. This means that insolubilization should be more efficient. For 10 example, a theoretical calculation will show that an equimolar mixture (based on monomer composition) of "KTFR" and hexaphenyldilead, which is about a 1% solution, should absorb about 15% more energy than "KTFR" alone, reducing the gel dose by a corresponding amount. However, in this instance the theory fails to predict experimental results; in fact, such a mixture reduces the gel dose by about 15 half. It is not known whether the theory is defective in some unknown manner or whether the additive participates in the crosslinking reaction in some undefined way; presumably, the theory is defective in not taking the unknown additive participation into account.

20 Following is a representative list of organometallic compounds which are effective in the embodiments:

Group III:

cyclopentadienylthallium

Group IV:

hexaphenyldilead

dibutyltin maleate

tetracyclohexyltin

divinyldibutyltin

Group V:

triphenylarsine

triphenylstilbene

triphenylbismuth

35 The metallic moieties in these compounds all qualify as heavy metals, and the organic moieties ensure their solubilities in the system. It will be appreciated that a variety of other compounds will meet these requirements. The organic radical of the organometallic compound is typically an alkyl, an aryl, or an alkyl-aryl radical.

40 Not all organometallics, however, are either operative or helpful. For example, compounds of mercury (a transition metal of Group 2b) such as phenylmercuric acetate and mercuric dibenzoate were not effective. Further, the compounds triphenyl-lead acetate, butyltin trichloride, and dibutyltin dilaurate did not meet the solubility requirements. Appropriately soluble compounds of aluminium could be expected to have a minor effect on sensitivity, but its atomic number is too small for it to be significant for electron capture. As will be seen from the Examples, the operable compounds are not all equivalents; some are significantly better than others.

45 While the dramatic decrease in gel dosage provided by these additives is in itself significant, it is not a necessary conclusion that the improvement will be of the same magnitude when the flux density necessary to expose a resist to a thickness of 3000 Å or 4000 Å is considered. More surprisingly, the magnitude of improvement is increased under these conditions. The following specific Examples I—VII will illustrate this. Similarly, when an additive such as a second group additive causes a large number of free radicals to be formed at each collision of an electron with a molecule, then it is not unreasonable to expect that the number of molecules crosslinked at each such energy transfer site will be higher. The problem, as noted above, is to add compounds that will not react spontaneously. While increased crosslinking could be expected with proper additive selection, the magnitude of improvement achieved with the above-noted compounds is quite remarkable. In particular, a five-fold reduction in the dose density required to fully expose a 4000 Å film is achieved. The improvement is not linear; the gel dose is reduced little if at all by using the additives. These facts are all clearly shown in the following specific Examples VIII—IX.

60 A further requirement of the additive is that it be soluble in the solvent system employed with the resist. The three noted compounds of the second group of the additives satisfy this requirement.

Both "KPR" and "KTFR" are supplied dissolved in a solvent. With the latter composition, a "KTFR" thinner may also be employed; this acts merely to reduce

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viscosity and produce a thinner film. The solvent system used for "KPR" is 86—87% chlorobenzene and 13—14% cyclohexanone. The "KTFR" solvent system is 12% ethylbenzene, 82% mixed xylenes and 6% methylcellosolve. Both systems also contain a sensitizer; in KTFR this is believed to be 2,6 bis (p-azidobenzilidene)-4-methylcyclohexanone. The "KTFR" thinner is primarily mixed xylenes.

To establish a basis for comparison, tests were first made with "KPR" and "KTFR" without any additives. "KPR" 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 6,000 Å thick. The coated plate was then placed in a vacuum chamber and radiated with electrons accelerated at 15 KV. The plate was developed with "KPR" developer and baked at 150°C. for 10 minutes. The following results were obtained:

- Flux needed to record an image (gel dose) =  $1.1 \times 10^{-6}$  coul/cm<sup>2</sup>.
- Flux needed to form 3,000 Å thick resist layer =  $6 \times 10^{-6}$  coul/cm<sup>2</sup>.
- Flux needed to form maximum thickness (after development, 4,000 Å) resist =  $10 \times 10^{-6}$  coul/cm<sup>2</sup>.

"KTFR" was mixed with "KTFR" thinner in a 1 to 3 ratio and the mixture applied to a chromium coated glass plate (or, alternatively, to a silicon slice onto which a 18,000 Å SiO<sub>2</sub> layer had been grown), and then spun to a thickness of 8,000 Å. After baking at 150°C. for 10 minutes, the film was 6,000 Å thick. The coated plates were then put into a vacuum chamber and radiated with 15 KV electrons. The plate was developed with "KTFR" developer and "KTFR" rinse, and baked at 150°C. for 10 minutes. The following results were found:

- Flux needed to record image (gel dose) =  $0.9 \times 10^{-6}$  coul/cm<sup>2</sup>.
- Flux needed to form 3000 Å film =  $4 \times 10^{-6}$  coul/cm<sup>2</sup>.
- Flux needed to form maximum (4000 Å) thickness =  $7.5 \times 10^{-6}$  coul/cm<sup>2</sup>.

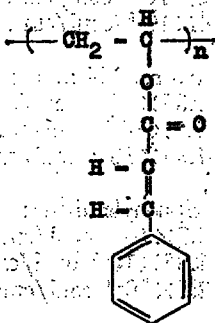
Under identical conditions, but with 5 KV electrons, the dose densities require to exposed "KTFR" films are:

- $0.5 \times 10^{-6}$  coul/cm<sup>2</sup>.
- $0.75 \times 10^{-6}$  coul/cm<sup>2</sup>.
- $2 \times 10^{-6}$  coul/cm<sup>2</sup>.

The following Examples directed to a small number of organometallic compounds show the improvements obtainable with the first group additives.

#### Example I

A saturated solution was prepared containing (~2%) of dibutyltin maleate in a photoresist solution including dimers of vinyl cinnamate having a principle constituent of



(1)

and the exact same procedure was followed as outlined above. Results with 15 KV electrons were as follows:

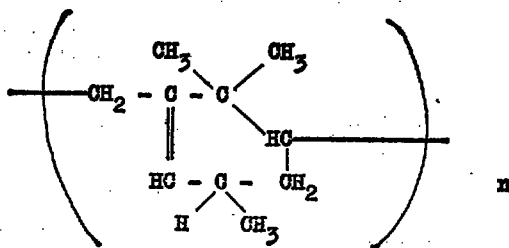
- $1.0 \times 10^{-6}$  coul/cm<sup>2</sup>.
- $1.5 \times 10^{-6}$  coul/cm<sup>2</sup>.
- $2.2 \times 10^{-6}$  coul/cm<sup>2</sup>.

It will be noted that with this additive, the improvement in gel dose was only nominal (about 10%), but was substantial for exposure to 3000 Å and 4000 Å.

FIG. 1 graphically illustrates the improvement in sensitivity achieved by using dibutyltin maleate as an additive. It also illustrates that dibutyl maleate, by itself, has no effect on sensitivity.

#### Example II

The same tests were carried out on a film prepared from a saturated solution (~1%) of hexaphenyldi-lead in a photoresist solution including polymerised isoprene dimers and having a principle constituent of



and further including a thinner. Results with 15 KV electrons were as follows:

- a)  $0.5 \times 10^{-6}$  coul/cm<sup>2</sup>.
- b)  $1.0 \times 10^{-6}$  coul/cm<sup>2</sup>.
- c)  $1.5 \times 10^{-6}$  coul/cm<sup>2</sup>.

Here, the reduction in gel dosage was 45%, and the reduction in dosage for a 4000 Å film was 5-fold. This is the most effective additive known.

FIG. 2 illustrates the rather dramatic increase in sensitivity in the above solution when hexaphenyldi-lead is used as an additive.

#### Examples III—VII

The standard procedures were repeated on five other additives in "KTR" and thinner, with 15 KV electrons, and concentrations and results as set forth below.

##### III. 1% tetracyclohexyltin:

- (a)  $0.5 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (b)  $2 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (c)  $4 \times 10^{-6}$  coul/cm<sup>2</sup>.

##### IV. 2% triphenylbismuth:

- (a)  $0.85 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (b)  $1.5 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (c)  $1.85 \times 10^{-6}$  coul/cm<sup>2</sup>.

##### V. 2% triphenylstilbene:

- (a)  $0.7 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (b)  $1.85 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (c)  $2.5 \times 10^{-6}$  coul/cm<sup>2</sup>.

##### VI. 2% triphenylarsine:

- (a)  $0.7 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (b)  $0.9 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (c)  $1.85 \times 10^{-6}$  coul/cm<sup>2</sup>.

##### VII. 1% cyclopentadienylthallium:

- (a)  $0.5 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (b)  $2 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (c)  $3 \times 10^{-6}$  coul/cm<sup>2</sup>.

The magnitude of improvement brought about by each of the additives is readily seen in Table I, where the percent reduction in dose for each of the three levels, as compared to the photoresist without any additives, is set forth.

| 5  | Example | TABLE I<br>Reduction in Dose, Pct. |            |            | 5  |
|----|---------|------------------------------------|------------|------------|----|
|    |         | (a) Gel Dose                       | (b) 3000 Å | (c) 4000 Å |    |
|    | I.      | 9.1                                | 75         | 78         |    |
|    | II.     | 45                                 | 75         | 80         |    |
|    | III.    | 45                                 | 50         | 47         |    |
| 10 | IV.     | 5.5                                | 63         | 75         | 10 |
|    | V.      | 22                                 | 54         | 67         |    |
|    | VI.     | 22                                 | 77         | 75         |    |
|    | VII.    | 45                                 | 50         | 60         |    |

It will be noted that one of the effects of the organometallic additives of the embodiments is to increase the slope of the plot of resist thickness vs. dose density to near infinity near the gel point (see FIGS. 1 and 2). By using the minimum dose density needed to achieve the desired thickness, back-scattered electrons or scattered primary electrons are minimized if not eliminated, and resolution capability of the resist is correspondingly increased. Under these conditions, an edge definition of about 300 Å can be expected as an upper limit. This is significantly better than previously reported definition.

It will be further noted by comparing the "KTFR" radiated with 5 and 15 KV electrons, that the 5 KV samples required less energy at all three stages.

The following Examples directed only to three compounds show the improvements which may be obtained with the second group additives.

#### Example VIII

A 5% solution of benzophenone in KPR is prepared. The three tests noted above are carried out (with 15 KV electrons). The results are as follows:

- |    |                                                 |    |
|----|-------------------------------------------------|----|
| 30 | (a) $1.0 \times 10^{-6}$ coul/cm <sup>2</sup> . | 30 |
|    | (b) $1.5 \times 10^{-6}$ coul/cm <sup>2</sup> . |    |
|    | (c) $2.0 \times 10^{-6}$ coul/cm <sup>2</sup> . |    |

#### Example IX

A 1% solution of benzophenone in a thinned (1 to 3) "KTFR" solution is prepared. Dose densities for the three tests with 15 KV electrons were as follows:

- |    |                                                  |    |
|----|--------------------------------------------------|----|
| 35 | (a) $0.5 \times 10^{-6}$ coul/cm <sup>2</sup> .  | 35 |
|    | (b) $1.0 \times 10^{-6}$ coul/cm <sup>2</sup> .  |    |
|    | (c) $1.75 \times 10^{-6}$ coul/cm <sup>2</sup> . |    |

It will be further noted by comparing the "KTFR" radiated with 5 and 15 KV electrons, that the 5 KV samples required less energy at all three stages. It is quite true, in fact, that lower energy electrons act much more efficiently than higher energy electrons; on the average, about 2.5 times the number of molecules at each energy transfer point will react at 5 KV than will at 15 KV. It would seem appropriate, then, to utilize lower energy electrons, but control of the size of the beam is more difficult at low energies. If very high potentials are used (+ 20 KV) the efficiency of crosslinking drops too low and back-scatter can become a significant problem. For these reasons, a 15 KV accelerating potential is preferred.

#### WHAT WE CLAIM IS:—

1. A method of improving the sensitivity of a photoresist coating to electron radiation comprising coating a substrate with a solvent containing a photoresist composition suitable for the generation of a pattern and a sensitizer therefore, the photoresist composition including either dimers of vinyl cinnamate or a polymerized isoprene and the sensitizer being an organometallic compound having a metallic moiety selected from metals in Groups III, IV or V of the Periodic Table having an atomic number greater than 30, and being present in an amount of up to 5 per cent of the total composition so that the sensitivity of the photoresist coating to electron radiation is improved.

2. A method as claimed in claim 1, wherein the organometallic compound is



1,291,441

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The magnitude of improvement brought about by each of the additives is readily seen in Table I, where the percent reduction in dose for each of the three levels, as compared to the photoresist without any additives, is set forth.

TABLE I

| Example | Reduction in Dose, Pct. |            |            |
|---------|-------------------------|------------|------------|
|         | (a) Gel Dose            | (b) 3000 Å | (c) 4000 Å |
| I.      | 9.1                     | 75         | 78         |
| II.     | 45                      | 75         | 80         |
| III.    | 45                      | 50         | 47         |
| IV.     | 5.5                     | 63         | 75         |
| V.      | 22                      | 54         | 67         |
| VI.     | 22                      | 77         | 75         |
| VII.    | 45                      | 50         | 60         |

It will be noted that one of the effects of the organometallic additives of the embodiments is to increase the slope of the plot of resist thickness vs. dose density to near infinity near the gel point (see FIGS. 1 and 2). By using the minimum dose density needed to achieve the desired thickness, back-scattered electrons or scattered primary electrons are minimized if not eliminated, and resolution capability of the resist is correspondingly increased. Under these conditions, an edge definition of about 300 Å can be expected as an upper limit. This is significantly better than previously reported definition.

It will be further noted by comparing the "KTFR" radiated with 5 and 15 KV electrons, that the 5 KV samples required less energy at all three stages.

The following Examples directed only to three compounds show the improvements which may be obtained with the second group additives.

## Example VIII

A 5% solution of benzophenone in KPR is prepared. The three tests noted above are carried out (with 15 KV electrons). The results are as follows:

- (a)  $1.0 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (b)  $1.5 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (c)  $2.0 \times 10^{-6}$  coul/cm<sup>2</sup>.

## Example IX

A 1% solution of benzophenone in a thinned (1 to 3) "KTFR" solution is prepared. Dose densities for the three tests with 15 KV electrons were as follows:

- (a)  $0.5 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (b)  $1.0 \times 10^{-6}$  coul/cm<sup>2</sup>.
- (c)  $1.75 \times 10^{-6}$  coul/cm<sup>2</sup>.

It will be further noted by comparing the "KTFR" radiated with 5 and 15 KV electrons, that the 5 KV samples required less energy at all three stages. It is quite true, in fact, that lower energy electrons act much more efficiently than higher energy electrons; on the average, about 2.5 times the number of molecules at each energy transfer point will react at 5 KV than will at 15 KV. It would seem appropriate, then, to utilize lower energy electrons, but control of the size of the beam is more difficult at low energies. If very high potentials are used (+20 KV) the efficiency of crosslinking drops too low and back-scatter can become a significant problem. For these reasons, a 15 KV accelerating potential is preferred.

## WHAT WE CLAIM IS:—

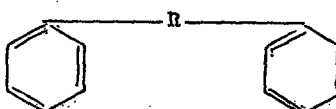
1. A method of improving the sensitivity of a photoresist coating to electron radiation comprising coating a substrate with a solvent containing a photoresist composition suitable for the generation of a pattern and a sensitizer therefore, the photoresist composition including either dimers of vinyl cinnamate or a polymerized isoprene and the sensitizer being an organometallic compound having a metallic moiety selected from metals in Groups III, IV or V of the Periodic Table having an atomic number greater than 30, and being present in an amount of up to 5 per cent of the total composition so that the sensitivity of the photoresist coating to electron radiation is improved.

2. A method as claimed in claim 1, wherein the organometallic compound is

selected from dibutyltin maleate, hexaphenyldilead, tetracyclohexyltin, triphenylbismuth, triphenylstilbene, triphenylarsine, cyclopentadienylthallium and divinyl dibutyltin.

3. A method as claimed in claim 1 or claim 2 wherein the organic radical of the organometallic compound is an alkyl, an aryl or an alkyl-aryl radical.

4. A method of improving the sensitivity of a photoresist coating to electron radiation comprising coating a substrate with a solvent containing a photoresist composition suitable for the generation of a pattern and a sensitizer therefore, the photoresist composition including either a polyvinyl cinnamate or a polymerized isoprene and the sensitizer being an organic compound having the general formula



wherein R is a radical having one or more carbon atoms and in which a carbon atom adjacent the phenyl ring is bonded to another atom by a double bond and being present in an amount of up to 5 per cent of the total composition so that the sensitivity of the photoresist coating to electron radiation is improved.

5. A method as claimed in claim 4 wherein the organic compound is benzophenone, benzyl or 1,4-diphenyl-1,3-butadiene.

6. A method as claimed in claim 4 or claim 5, wherein the organic compound is 1 per cent of the photoresist solution.

7. A method as claimed in any one of the preceding claims, wherein the solvent for the photoresist including dimers of vinyl cinnamate is a mixture of chlorobenzene and cyclohexanone.

8. A method as claimed in any one of claims 1 to 6, wherein the solvent for the photoresist including polymerized isoprene is ethylbenzene, mixed xylenes and methylcellulose.

9. A substrate having a photoresist coating thereon and sensitized according to any one of claims 1 to 8.

10. A method of improving the sensitivity of a photoresist coating to electron radiation substantially as hereinbefore described with reference to any one of the Examples.

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