

Positive Dye Photoresist Compositions with Orange-1 and Lake Red-D Dye:

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Abstract: Two novolac resins one with the mixture of ortho, meta and para cresol and other with the mixture of meta cresol and 2, 6-bis (hydroxyl methyl) -Para tertiary butyl phenol have been synthesized. 1-oxo -2-diazo naphthalene-5-sulfonyl chloride and its corresponding sulfonate esters with 2,3,4-trihydroxy benzophenone and phlorobenzophenone and corresponding sulphonamides with benzidine and 6,6' diamino-2,2'-dimethylbiphenyl have been synthesized. Two new azo dyes namely Orange-1 and Lake Red-D dye one containing sulphonic acid group and other containing carboxylic acid group have been synthesized. Photoresist films have been casted on silicon wafer by mixing novolac resin, sulfonate ester or sulphonamide of ortho naphthaquinone diazide and the corresponding dye into the solvent mixture of acetone, xylene and ethylacetate. After soft baking the photo resist films are irradiated with UV radiation exposure. Upon actinic radiation the exposed regions are soluble in aqueous alkaline developer.

Key Words: Novolac resin, 1-oxo-2-diazo naphthalene-5-sulfonyl chloride, sulfonate esters, sulphonamides, orange-1 dye, Lake Red-D dye, actinic radiation.

I. Introduction

Lithography is a technique used by the microelectronics industry in the fabrication of integrated circuits. In this context, the lithographic process involves using an exposure technique to transfer a pattern from a mask to a polymer film and finally to a semiconducting substrate. A variety of modes of exposure can be employed for this purpose including UV or X-ray radiation and electron or ion-beams. The photolithographic process employs UV radiation and is the primary technique currently used in industrial applications. Briefly, a thin film of a photosensitive polymer, termed a resist, which has been spin-coated onto a semiconducting substrate, is exposed to light through a mask. The mask is composed of a pattern which prevents light from reaching certain regions of the resist and allows it in other regions. Interaction of light with the resist includes a chemical change, creating a latent image of the pattern from the mask, in the resist. This photo induced chemical change causes a difference in the dissolution rate between exposed and unexposed regions. Development of the resist with an appropriate solvent selectively dissolves the exposed or unexposed regions, producing positive or negative tone images respectively. After the development step, regions of the substrate are left exposed, allowing them to be etched, thereby transferring the pattern to the substrate. Finally, the remaining resist is washed away to leave the bare, patterned substrate.

The first positive photo resist were composed of alkali soluble phenol-formaldehyde novolac resins together with light-sensitive materials. Examples of the light sensitive materials are diazoquinones (DAQs) such as the sulfonate and carboxylate esters and the sulfon and carbonamides obtained by reacting respectively ortho naphthaquinone diazide sulfonyl and carbonyl halides with hydroxyl, polyhydroxy, amino and polyamino ballast compounds. The resins and sensitizers are dissolved in an organic casting solvent or mixture of casting solvents and are applied as a dried thin film or coating to a substrate suitable for the particular application desired.

The resin component of these photoresist formulations is soluble in aqueous alkaline solutions, but the admixed naphthaquinone sensitizer acts as a dissolution inhibitor with respect to the resin. Upon exposure of selected areas of a coated substrate to actinic radiation, the sensitizer undergoes a radiation induced chemical transformation, and the exposed areas of the coating are rendered more soluble than the unexposed area. The main photoproduct of the diazonaphthaquinone is base soluble, thereby allowing solubilization of the resist after exposure to light. Upon absorption of a photon, the diazonaphthaquinone loses nitrogen to form a carbene which undergoes Wolff rearrangement to a ketene. The ketene is attacked by water to form indene carboxylic acid.

This difference in solubility rates causes the exposed areas of the photoresist coating to be dissolved when the substrate is immersed in alkaline developing solution, while the unexposed areas are largely unaffected. This produces a positive relief resist pattern on the substrate. Thus, an etched pattern can be created on the substrate which corresponds to the pattern of the mask, stencil, template etc. The relief pattern of photoresist on the substrate produced by the method just described is useful for various applications, including the manufacture of miniaturized integrated electronic circuit components.

The properties of a photoresist composition which are important in commercial practice include the photospeed of the resist, development contrast and resist resolution capability and resist sidewall angle or wall profile and resist adhesion. Increased photospeed is important for a photoresist, particularly in application where light of reduced intensity is employed such as in projection exposure techniques where the light is passed through a series of lenses and monochromatic filters.

Resist resolution refers to the capability of a resist system to reproduce with a given phototool the smallest multiple equal line features of a mask which is utilized during exposure. In many industrial applications, particularly in the manufacture of miniaturized electronic components, a photoresist is required to provide a high degree of resolution for very narrow lines.

The positive photoresist compositions and processes provided in this invention dramatically improve performance properties on reflective semiconducting substrates while maintaining adequate photospeed. Photoresist absorbance in these compositions is increased by the addition of two dyes mainly orange-1 and Lake Red-D dye. These two dyes enhance the dissolution rate of the exposed photoresist in developer because the dyes contain one sulfonic acid and one carboxylic acid group respectively.

II. Experimental

2.1. Preparation of Novolac Resin:

2.1.1. Preparation of Novolac Resin from the mixture of ortho, meta and para cresol:

A one liter four-neck resin kettle equipped with a stirrer, heating source, thermometer, variable reflux ratio distilling head and a nitrogen inlet tube was charged with 70.0g meta cresol, 84.0g para cresol, 9.0g ortho cresol, 17.0g of 36.9% formalin, 5ml deionized water and 3.0g oxalic acid dihydrate. The mixture was heated to about 60⁰c at which point an exothermic condensation reaction ensued. When the reaction mixture temperature reached about 100⁰c, 68.0g of 36.9% formalin was added in about 30 minutes. The reaction was then allowed to continue for about 4 hours at reflux temperature. The more volatile components in the reaction mixture were removed by distillation at ambient pressure under a constant flow of nitrogen. When the temperature of the reaction mixture reached about 220⁰c, a partial vacuum pressure was applied and was gradually increased until a maximum vacuum of 7 mm Hg was achieved, and the mixture was at about 228⁰c. The liquified resin remaining in the kettle was poured into a tray under nitrogen and allowed to cool and solidify.

2.1.1. Preparation of Novolac Resin with the mixture of meta cresol and 2,6-Bis (hydroxymethyl) para tertiary butyl phenol:

A phenolic resin rich in alternating phenolic copolymer block segments was formed by 52.0g of meta cresol, 67.2g of 2, 6-bis (hydroxymethyl) PTBP and 2 g oxalic acid dihydrate in a solvent mixture of 4 ml deionized water and 20 ml ethyl cellosolve acetate. The reaction mixture was heated to about 70⁰c to initiate the reaction forming the copolymer block segments. At 102⁰c, 3.3g of 36.9% formaldehyde was added in 5 minutes to the reaction mixture to form substantially meta cresol formaldehyde block segments and to chemically bond these segments to the previously formed copolymer blocks. After heating the mixture at reflux for 3 hours, the amount of heat was increased to remove the water and solvent by distillation. Partial vacuum was applied at about 220⁰c and gradually increased to 4 mm Hg to remove the unreacted monomers. The copolymer was poured from the reaction kettle and allowed to cool.

2.2 Preparation of 1-oxo-2-diazo naphthalene -5-sulfonyl chloride:

3.0g of sodium 1-diazo-1, 2-naphthaquinone-5-sulfonate was taken in a foil covered flask. 14 ml of chlorosulfonic acid was carefully added to the flask so as to maintain the reaction temperature below 60⁰c. The reaction mixture was heated with stirring for 30 minutes at 65⁰-70⁰c. The mixture was then allowed to cool in an ice bath and added 100ml cold water dropwise such that the reaction temperature did not exceed 75⁰c. The yellow precipitate of 1-diazo-1, 2-naphthaquinone-5-sulfonyl chloride was collected with vacuum filtration.

2.3 Preparation of sulfonate esters and sulfonamides of 1-oxo-2-diazo naphthalene-5-sulfonyl chloride:

2.3.1. Preparation of ortho naphthaquinone diazide sulfonate ester of 2,3,4-trihydroxybenzophenone:

To a 250 ml flask equipped with a constant temperature bath, thermometer, magnetic stirrer were added 5.5g (0.025 mols) of 2,3,4-trihydroxybenzophenone, 7.5g (0.028 mols) of 1-oxo-2-diazonaphthalene-5-sulfonyl chloride and 100 ml of reagent grade acetone. While the mixture was maintained at 30⁰c; 14.25g of 12% sodium carbonate was added dropwise over 5 minutes. After the base addition, the reaction mixture was allowed to stir for 30 minutes at about 30⁰c. 2.5 ml of concentrated hydrochloric acid was then slowly added to the mixture while keeping its temperature below 30⁰c. The reaction solution was filtered to remove the bulk of sodium chloride and the filtrate was added to 500 ml 1% hydrochloric acid. The precipitated solid was stirred for 1 hour, filtered and collected.

2.3.2. Preparation of ortho naphthaquinone diazide sulfonate ester of phlorobenzophenone:

To a 250 ml flask equipped with a constant temperature bath, thermometer, magnetic stirrer were added 11.5g (0.05 mols) of phlorobenzophenone, 13.4g (0.05 mols) of 1-oxo-2-diazo naphthalene-5-sulfonyl chloride and 115 ml of reagent grade acetone. While the mixture was maintained at 30⁰c, 28g of 12% sodium carbonate was added dropwise over 10 minutes. After the base addition, the reaction mixture was allowed to stir for 40 minutes at 30⁰c. 5ml of concentrated hydrochloric acid was then slowly added to the mixture while keeping its temperature at 30⁰c. The reaction solution was filtered to remove bulk of sodium chloride and the filtrate was added to 1000 ml 1% hydrochloric acid. The precipitated solid was stirred for 1 hour, filtered and collected.

2.3.3. Preparation of orthonaphthaquinone diazide sulphonamide of benzidine:

In a 250 ml flask equipped with constant temperature bath, thermometer, magnetic stirrer were added 13.4 g (0.05 mols) diazonaphthaquinone sulfonyl chloride, 9.2 g (0.05 mols) benzidine and 100 ml of tetrahydrofuran. The mixture was stirred for 30 minutes at room temperature. To this reaction mixture 6 ml triethylamine was added dropwise with stirring and allowed to stir for 1 hour. 500 ml of cold water was added to the reaction mixture and chilled in an ice-bath to precipitate out the product. The product was collected using vacuum filtration, washed it with cold water until the washings were colourless, air dried and washed with petroleum ether.

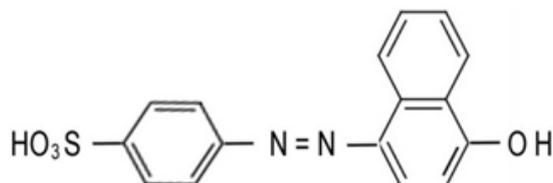
2.3.4. Preparation of ortho naphthaquinone diazide sulphonamide of 6, 6'-diamino-2, 2'-dimethylbiphenyl:

In a 250 ml flask equipped with constant temperature bath, thermometer, magnetic stirrer were added 13.4g (0.05 mols) diazonaphthaquinone sulfonyl chloride, 10.60g (0.05 mols) 6,6'-diamino-2,2'-dimethylbiphenyl and 115 ml tetrahydrofuran. The mixture was stirred for 40 minutes at room temperature. To this reaction mixture 6 ml triethylamine was added dropwise with stirring and allowed to stir for 1 hour. The reaction mixture was then poured into 500 ml of cold water and chilled in an ice-bath to precipitate out the product. The product was collected using vacuum filtration, washed it with cold water until the washings were colourless, air dried and washed with petroleum ether.

2.4. Preparation of azo dye:

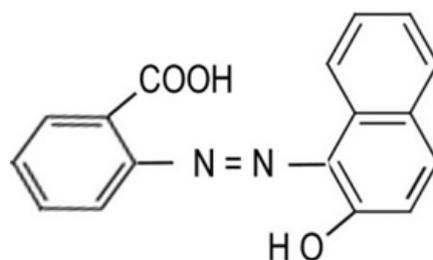
2.4.1. Preparation of orange-1:

2.6 g of sulphanilic acid 0.7 g of sodium carbonate and 25 ml of water were taken in a 250 ml beaker. The mixture was warmed until a clear solution was obtained. The mixture was then cooled to 5⁰c. Now a solution was prepared by adding 1.0 g sodium nitrite in 10 ml water in a 100 ml beaker. The sodium nitrite solution were added to the above reaction mixture. Now a solution of 3.0 ml concentrated hydrochloric acid and 15 g ice with 10 ml water was prepared in a 100 ml beaker. The above prepared solution were added very slowly with stirring into 250 ml beaker. 1.8 g of 1-naphthol in 10 ml cold 10% sodium hydroxide with 25 ml of water were dissolved in a 500 ml beaker. The mixture was cooled to 5⁰c. In this solution the above prepared solution was added with stirring. Dyestuff separated out as a crystalline paste. After 10 minutes, the mixture was heated until all the solid dissolved. Now 5 g sodium chloride was added to the mixture and warmed. The solution was allowed to cool for 30 minutes and then in ice-bath until crystallization completed. The dye was filtered and dried.



2.4.2. Preparation of Lake Red-D dye:

2.6 g anthranilic acid, 0.7 g of sodium carbonate and 25 ml water were taken in a 250 ml beaker. The mixture was warmed until a clear solution was obtained. The mixture was then cooled to 5⁰c. Now a solution of 1.09 g sodium nitrite in 10ml water was added to the above prepared solution. Now a solution of 3 g concentrated hydrochloric acid and 15 g ice with 10 ml water was prepared in a 100 ml beaker. The above prepared solution was added very slowly with stirring to 250 ml beaker. 1.8 g of 2-naphthol was dissolved in 10 ml 10% sodium hydroxide in a 500 ml beaker. The mixture was cooled to 5⁰c. The diazonium salt solution was then added to the solution of 2-naphthol with stirring. Dyestuff separated out as a crystalline paste. After 10 minutes the mixture was heated until all the solid dissolved. 5 g of sodium chloride was then added and warmed. The solution was allowed to cool for 30 minutes then in ice-bath until crystallization completed. The dye was filtered and dried.



2.5 Photoresist compositions with different dye compounds:

Example-1

A Photoresist composition was prepared by dissolving 2.4 g of the naphthaquinone diazide sulfonate ester, 0.2 g of the orange-1 dye and 9.9 g of the novolac resin into a solvent mixture of 22.4 g of acetone, 11.2 g of xylene and 3.7 g of ethylacetate. The resist composition was evaluated by dip coating a film onto silicon wafer. The film was then baked at 100⁰c for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region, in any desired exposure pattern produced by using suitable masks, stencils, templates etc. The exposed, resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

Example-2

A Photoresist composition was prepared by dissolving 2.4 g of the naphthaquinone diazide sulfonate ester, 0.2 g of the Lake Red-D dye and 9.9 g of the novolac resin into a solvent mixture of 22.4 g of acetone, 11.2 g of xylene and 3.7 g of ethylacetate. The resist composition was evaluated by dip coating a film onto silicon wafer. The film was then baked at 100⁰c for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region, in any desired exposure pattern produced by using suitable masks, stencils, templates etc. The exposed, resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

Example-3

A photoresist composition was prepared by dissolving 2.4 g of the naphthaquinone diazide sulfonate ester, 0.1 g of the orange-1 dye and 0.1 g of the Lake Red-D dye and 9.9 g of the novolac resin into a solvent mixture of 22.4 g of acetone, 11.2g of xylene and 3.7 g of ethyl acetate. The resist composition was evaluated by dip-coating a film onto silicon wafer. The film was then baked at 100⁰c for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region in any desired exposure pattern produced by using suitable masks, stencils, templates etc. The exposed, resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

Example-4

A photoresist composition was prepared by dissolving 2.4 g of the naphthaquinone diazide sulphonamide, 0.2 g of the orange-1 dye and 9.9 g of the novolac resin into a solvent mixture of 22.4 g of acetone, 11.2g of xylene and 3.7 g of ethyl acetate. The resist composition was evaluated by dip-coating a film onto silicon wafer. The film was then baked at 100⁰c for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region in any desired exposure pattern produced by using suitable masks, stencils, templates etc. The exposed, resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

Example – 5

A photoresist composition was prepared by dissolving 2.4 g of the naphthaquinone diazide sulphonamide, 0.2g of the Lake Red-D dye and 9.9 g of the novolac resin into a solvent mixture of 22.4g of acetone, 11.2g of xylene and 3.7g of ethylacetate. The resist composition was evaluated by dip-coating a film onto a silicon wafer. The film was the baked at 100⁰C for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region, in any desired exposure pattern produced by using suitable masks, stencils, templates etc. The exposed, resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds until all the resist coating was dissolved from the image wise exposed areas.

Example –6

Aphotoresist composition was prepared by dissolving 2.4g of the naphthaquinone diazide sulphonamide, 0.1 g of the orange-1 dye, 0.1g of the Lake Red- D dye and 9.9 of the novolac resin in to a solvent mixture of 22.4g of acetone, 11.2 g of xylene and 3.7g of ethyl acetate. The resist composition was evaluated by dip coating a film onto a silicon wafer. The film was then baked at 100⁰ C for 30 minutes in a convection oven. The coated substrate was then image wise exposed to radiation in the near ultra violet region, in any desired exposure pattern produced by using suitable masks, stencils, templates etc. The exposed, resist coated substrate was then contacted with aqueous alkaline developer for 60 seconds, until all the resist coating was dissolved from the image wise exposed areas.

III. Result and Discussion:

The following combination of properties of the novel dyed positive photoresist compositions of the present invention are distinctly better than the photoresist compositions of the prior art:(1)The novel dyes namely orange-1 and LakeRed-D dye are soluble in aqueous alkaline developer and does not significantly inhibit the dissolution rate of the exposed photoresist film in aqueous alkaline developers,(2)The dye does not significantly harm deep-UV curing processes of the photoresist film.(3) The dyed photoresist compositions have substantially better resolution,(4) The dyed photoresist compositions require less exposure energy than prior dyed photoresist compositions,(5)The novel dyes are non-volatile and are not readily sublimed from the resist film and (6)The novel dyed photoresist composition are stable for at least one year with out forming precipitates.

The new positive photoresist compositions containing aqueous alkaline soluble orange-1 and Lake Red-D dyes which have the advantage of high resolution, improved photospeed, deep-UVcurable,and high absorbance, excellent stability ,non volatility and patterning method using the compositions of the present invention.

The present invention provides novel photoresist compositions which contain highly absorbant actinic orange-1 and LakeRed-D dyes highly soluble in both casting solvent and aqueous alkaline developer,high resolution novolac resin,and high resolution photoactive component with several diazoquinone groups per molecule dissolved into safer solvents with high solvency power. The compositions of the present invention have the advantages of high resolution capability,improved control of reflection, effects high unexposed film thickness remaining after development ,increased photoresist stability and low required exposure dose.Enhancing the actinic absorbance of positive photoresist diminishes undesirable reflection phenomena.The absorbance at the wavelength of irradiation can be enhanced through the addition of dye to the photoresist.The optimal dye should have the following properties:highly absorbing from 365nm to436nm in the spectral region to allow use of the same composition on a variety of photolithographic exposure equipment,high solubility in the photoresist solvent, self lifeof at least 6 months,solubility in aqueous alkaline developers,does not sublime significantly during baking processing,does not significantly harm deep-UV curing processing and does not reduce significantly the dissolution rate of exposed photoresist in developer solution.

The orange-1 and Lake Red-D dyes used in the compositions of the present invention have good solubility in the casting solvent and aqueous alkaline developer. Solubility in the casting solvent is a complex chemical phenomenon thatdepends upon the chemical nature of the individual photoresist components,including the chemical functionality, type and nature of bonding,polarity,flexibility and shapes of the solvent and dye molecules. Solubility in the aqueous alkaline developer is primarily determined by the type and the number of the acidic hydrophilic groups. Examples of acidic hydrophilic substituents include acid groups and hydroxyl groups. The location and intensity of the ultraviolet/visible absorption spectrum of the dye is determined by the electronic nature of the individual dye molecule and its interaction with the other molecules in the photoresist compositions .

The most preferred solvent composition of this invention are ,blends of acetone,xylene and ethyl acetate.These solvents give a useful combination of low required exposure dose,good solvency,low toxicity useful volatility.

The most preferred compositions of the present invention include from about 75 to about 92 percent of a mixture of base soluble phenolic resin and a dye or mixture of dyes,the proportions by weight of said dyes are about 0.4 percent to about 8 percent of the weight of resin and from about 8 to about 25 percent of a ortho quinine diazide sulfonate ester or sulphonamide.

IV. Conclusion

This article summarizes the recent development of positive dye photoresist composition with two novel azo dyes namely orange-1 and Lake-Red D dye.The dyes contain one sulphonic acid group and one carboxylic acid group respectively.This novel positive dyed photoresist are distinctly better than the photoresist composition of the prior art.The novel two dyes namely orange-1 and Lake Red-D dye are soluble in both the

casting solvent and also in aqueous alkaline developer. The dyes do not significantly harm deep UV curing process of photoresist film. The novel dyed photoresist compositions have substantially better resolution and require less exposure energy. The novel dyes are non-volatile and are not readily sublimed from the resist film. The mixture of casting solvent is new and cheaper. These solvents have little toxicity, good solvency and useful volatility. The new aqueous alkaline developer used here is 0.25(M) tetramethylammonium hydroxide which does not form scum on the exposed semiconductor substrates.

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