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(54) Title: ANTIREFLECTIVE COATING FOR PHOTORESIST COMPOSITIONS

(57) Abstract: The present invention relates to a novel antireflective coating solution and a process for its use in photolithography. The antireflective coating solution comprises a novel polymer and an organic solvent or mixture of solvents, where the novel polymer comprises a unit containing a dye that absorbs from about 180 nm to about 450 nm and does not contain a crosslinking group.

Description

Antireflective Coating for Photoresist Compositions

Background of the Invention

The present invention relates to novel antireflective coating compositions and their use in forming a thin layer between a reflective substrate and a photosensitive coating. Such compositions are especially useful in the fabrication of semiconductor devices by photolithographic techniques. Furthermore, the novel polymer may be used as an absorbing polymer in photoresist formulations.

Photoresist compositions are used in microlithography processes for making miniaturized electronic components such as in the fabrication of computer chips and integrated circuits. Generally, in these processes, a thin coating of film of a photoresist composition is first applied to a substrate material, such as silicon wafers used for making integrated circuits. The coated substrate is then baked to evaporate any solvent in the photoresist composition and to fix the coating onto the substrate. The baked coated surface of the substrate is next subjected to an image-wise exposure to radiation.

This radiation exposure causes a chemical transformation in the exposed areas of the coated surface. Visible light, ultraviolet (UV) light, electron beam and X-ray radiant energy are radiation types commonly used today in microlithographic processes. After this image-wise exposure, the coated substrate is treated with a developer solution to dissolve and remove either the radiation-exposed or the unexposed areas of the photoresist.

The trend towards the minitiarization of semiconductor devices has led to the use of sophisticated multilevel systems to overcome difficulties associated with such minitiarization. The use of highly absorbing antireflective coatings in photolithography is a simpler approach to diminish the problems that result from back reflection of light from highly reflective substrates. Two deleterious effects of back reflectivity are thin film interference and reflective notching. Thin film interference results in changes in critical linewidth dimensions caused by variations in the total light intensity in the resist film as the thickness of the resist changes. Variations of linewidth are proportional to the

swing ratio (S) and therefore must be minimized for better linewidth control. Swing ratio is defined by:

$$S = 4(R_1R_2)^{1/2}e^{-\alpha D}$$

where,

R_1 is the reflectivity at the resist/air or resist/top coat interface,

R_2 is the reflectivity at the resist/substrate interface,

α the resist optical absorption coefficient, and D is the film thickness.

Antireflective coatings function by absorbing the radiation used for exposing the photoresist, that is, reducing R_2, and thereby reducing the swing ratio. Reflective notching becomes severe as the photoresist is patterned over substrates containing topographical features, which scatter light through the photoresist film, leading to linewidth variations, and in the extreme case, forming regions with complete resist loss.

In the past dyed photoresists have been utilized to solve these reflectivity problems. However, it is generally known that dyed resists only reduce reflectivity from the substrate but do not totally eliminate it. In addition, dyed resists may cause reduction in the lithographic performance of the photoresist, together with possible sublimation of the dye and incompatibility of the dye in resist films. In cases where further reduction or elimination of the swing ratio is required, an antireflective coating is applied to the substrate prior to coating with the photoresist and prior to exposure. The resist is exposed imagewise and developed. The antireflective coating in the exposed area is then etched, typically in an oxygen based plasma, and the resist pattern is thus transferred to the substrate. The etch rate of the antireflective film should be relatively high so that the antireflective film is etched without excessive loss of the resist film during the etch process.

Antireflective coatings containing a dye for absorption of the light and an organic polymer to give coating properties are known. However, the possibility of sublimation and diffusion of the dye into the photoresist layer during the heating process can make these types of antireflective compositions undesirable.

Polymeric organic antireflective coatings are known in the art as described in EP 583,205 and US 5,525,457 and incorporated herein by reference. However, these antireflective films are cast from organic solvents, such as cyclohexanone and cyclopentanone. The potential hazards of working with organic solvents, have led to the development of the antireflective coating composition of the instant invention, where the

solid components of the antireflective coating are both soluble and spin castable from solvents having lesser toxicity hazards. The preferred solvents that are known in the semiconductor industry to have low toxicity among others are propylene gycol monomethyl etheracetate (PGMEA), propylene gycol monomethylether (PGME), and ethyl lactate.

In another embodiment, by the judicious choice of electrophilic substituents and comonomers, the polymer of the present invention is castable from water. Water based coatings are not only preferred but also provide a distinct advantage in the semiconductor industry due to their ease of handling.

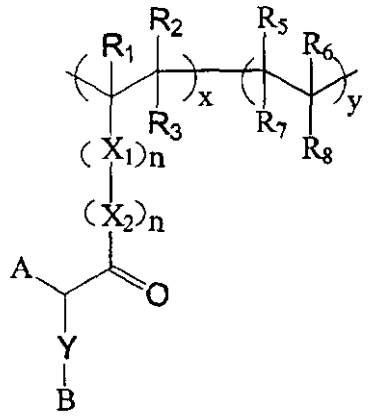
The polymeric coatings disclosed in US 5,652,297 and US 5,652,317 are soluble in the preferred solvents but contain a different pendant chromophore than the present invention. The chromophore disclosed in US 5,733,714 is similar to the present invention but the comonomer in US 5,733,714 contains a crosslinking group. It has now been unexpectedly found that both a homopolymer containing a similar pendant chromophore to the one disclosed in US714, and also a copolymer synthesized from a monomer containing the same pendant chromophore and a comonomer without a crosslinking group, also functions effectively as a bottom coat for the photoresist or as an additive in a photoresist. It has been found that in some instances it is preferable to have a polymer that does not contain a comonomer with a crosslinking group, since this crosslinking group could lead to instability or insolubility of the solution or the coating.

The polymer of the present invention contains a specific dye functionality, and, furthermore, the polymer may be a homopolymer or copolymerized with specific types of monomers that do not contain a crosslinking group. Good coatings are formed with the antireflective coating of the instant invention and, additionally, no intermixing is present between the antireflective coating and the photoresist film. The coating formed from this polymer also has good dry etching properties when used as a bottom coat for a photoresist, which enables a good image transfer from the resist to the substrate and good absorption characteristics to prevent reflective notching and linewidth variations.

Summary

The present invention relates to a novel antireflective coating composition and processes for its use in photolithography. The polymer of the antireflective coating composition comprises at least one unit with a dye and no crosslinking groups. The dye functionality is one that strongly absorbs radiation ranging from about 180nm

(nanometer) to about 450nm. The antireflective coating composition comprises a solvent and a polymer of the following structure:



where,

R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

R_5-R_8 do not have a crosslinking group and are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, hydroxyalkyl, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, hydroxy (C_1-C_{10}) alkyl, (C_1-C_{10})alkylOCOCH$_2$COCH$_3$, or R_7 and R_8 combine to form a cyclic group,

X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,

X_2 is S, S(C_1-C_{10}) alkyl , O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),

n is independently 0-2,

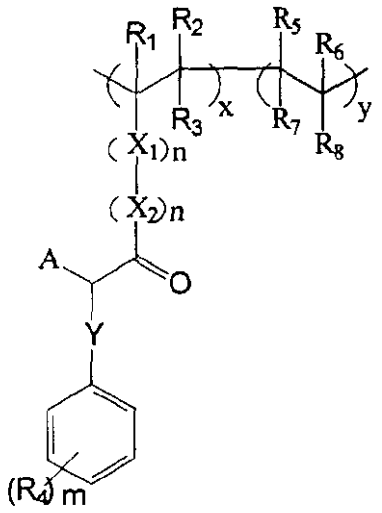
A is an electronwithdrawing group,

Y is a conjugated moiety e.g. N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

$x > 0$, and $y \geq 0$, and

B is selected from a 5-10 membered aromatic group, polyaromatic group or a heterocyclic aromatic group.

Preferably the polymer has the following structure,



where,

R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

R_5-R_8 do not have a crosslinking group and are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, hydroxyalkyl, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, hydroxy (C_1-C_{10}) alkyl, (C_1-C_{10})alkylOCOCH$_2$COCH$_3$, or R_7 and R_8 combine to form a cyclic group,

X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,

X_2 is S, S(C_1-C_{10}) alkyl , O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),

n is independently 0-2,

A is an electronwithdrawing group,

R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl,

Y is a conjugated moiety N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

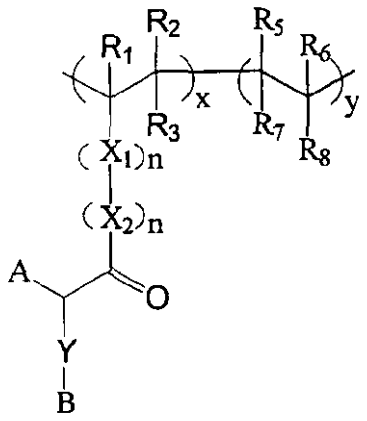
m = 1-5, $x > 0$, and $y \geq 0$.

The invention further comprises a process of forming an image on a substrate. The substrate is coated with the film of the antireflective coating of the instant invention and heated to remove any residual solvent and to insolubilize the coating. A film from a photoresist solution is then formed on top of the antireflective coating and further heated to substantially remove the photoresist solvent. The photoresist film is imagewise exposed through a mask with ultraviolet radiation ranging from about 180nm to about 450nm and processed in an aqueous alkaline developer to give a photoresist pattern. The substrate may be heated prior to and after the development step to give an image of superior quality. The exposed antireflective film can then be dry etched, usually in an oxygen plasma, with the photoresist pattern acting as an etch mask. In another embodiment of the invention, a silylating step is introduced after the development step and the prior to the etching step.

Detailed Description of the Invention

The coating compositions of the present invention comprise a polymer which may be either a homopolymer obtained by reacting a monomer containing a dye of a specific structure or a copolymer where the dye monomer is reacted with a monomer which does not contain a crosslinking group, and, furthermore, where the polymer thus obtained strongly absorbs ultraviolet light having a wavelength in the range of 180nm to about 450nm. The present invention further provides for a process of coating and baking the antireflective coating on a substrate and applying and imaging a photoresist film on top of the antireflective coating, and followed by etching of the antireflective coating.

The polymer of the instant invention is obtained by reacting at least one vinyl monomer containing a dye functionality to form a homopolymer or with at least one other vinyl monomer that does not contain a crosslinking group to form a copolymer. The dye functionality is one that strongly absorbs radiation ranging from about 180nm to about 450nm. The preferred types of dyed monomeric units that can be used are defined by the following structure:



Structure 1

where,

R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

R_5-R_8 do not have a crosslinking group and are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, hydroxyalkyl, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, hydroxy (C_1-C_{10}) alkyl, (C_1-C_{10})alkyl$OCOCH_2COCH_3$, or R_7 and R_8 combine to form a cyclic group,

X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,

X_2 is S, S(C_1-C_{10}) alkyl , O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),

n is independently 0-2,

A is an electronwithdrawing group,

Y is a conjugated moiety e.g. N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

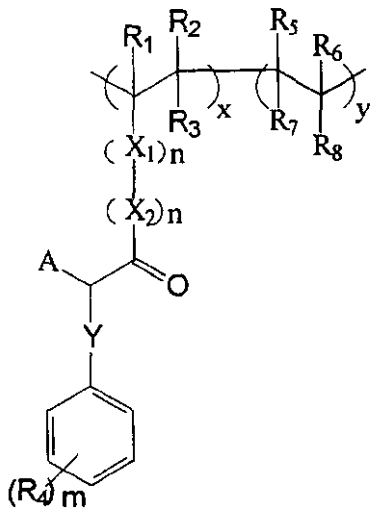
$x > 0$, and $y \geq 0$, and

B is selected from a 5-10 membered aromatic group, polyaromatic group or a heterocyclic group.

The pendant group, B, of the chromophore is an aromatic moeity, such as a substituted or unsubstituted 5-10 aromatic hydrocarbon ring, a substituted or unsubstituted polynuclear aromatic hydrocarbon ring, such as phenyl, naphthyl or

anthracyl rings, or substituted or unsubstituted heterocyclic aromatic groups, such as pyridine, indole, pyrazore, thiophene, etc.

Preferably, the polymer has the structure,



where,

R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

R_5-R_8 do not have a crosslinking group and are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, hydroxyalkyl, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, hydroxy (C_1-C_{10}) alkyl, (C_1-C_{10})alkylOCOCH$_2$COCH$_3$, or R_7 and R_8 combine to form a cyclic group,

X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,

X_2 is S, S(C_1-C_{10}) alkyl , O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),

n is independently 0-2,

A is an electronwithdrawing group,

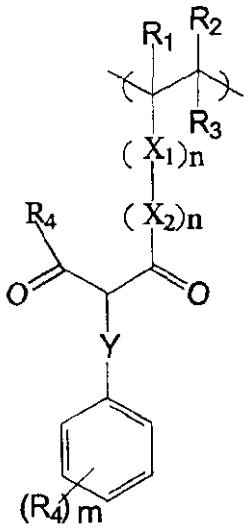
R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl,

Y is a conjugated moiety N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

m = 1-5, x > 0, and y ≥ 0.

The group A, is electron withdrawing, and is preferably COR_4, CN or CZ.

The more preferred structure for the dye unit is,



where,

R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,

X_2 is S, S(C_1-C_{10}) alkyl, O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),

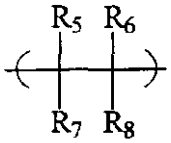
n=0-2,

R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl,

Y is a conjugated moiety e.g. N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy, and

m = 1-5.

In a preferred embodiment where the polymer of the present invention is used as a bottom coat that has to be etched by a plasma, a copolymer is preferred, where the copolymer has at least one dye unit of a Structure 1 and a unit of the following Structure 2:

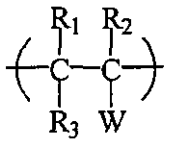


Structure 2

where,

R_5-R_8 are not a crosslinking group and are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where, Z is H or (C_1-C_{10}) alkyl, hydroxy (C_1-C_{10}) alkyl, (C_1-C_{10})alkylOCOCH$_2$COCH$_3$, or R_7 and R_8 combine to form a cyclic group, such as anhydride, pyridine or pyrollidone.

In another embodiment a hydrophilic monomeric unit that promotes water solubility in the copolymer is present in the polymer together with a unit containing a dye functionality, and, furthermore, where the hydrophilic monomer can be represented by the structure:



where,

R_1 to R_3 are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy and W is a hydrophilic group.

Examples of the hydrophilic group, W, are given here but are not limited to these: O(CH$_2$)$_2$-O-(CH$_2$)-OH, O(CH$_2$)$_2$-OH, (CH$_2$)$_n$-OH (where n=0-4), COO(C_1-C_4) alkyl, COOX and SO_3X (where X is H, alkali metal, ammonium, alkyl ammonium).

Other hydrophilic vinyl monomers that can also be used to form the polymer are, maleic anhydride, maleimide, vinyl pyridines, and vinyl pyrollidones.

The water soluble antireflective polymer can be synthesized by reacting any number of vinyl monomers containing at least one dye functionality described in Structure 1, any number of vinyl monomers that do not contain a crosslinking functionality (Structure 2) and/or any number of hydrophilic vinyl monomers. Mixtures of different dye monomers, different noncrosslinking monomers and different hydrophilic monomers can be polymerized to give an antireflective coating with the optimally desired lithographic and physical properties. Other unsaturated monomers can be added to the polymerization mixture that do not deteriorate the functional properties of the polymer. Examples of such unsaturated monomers are, maleic anhydride, vinyl acrylates, vinyl ethers, vinyl acrylamides, vinyl carboxylic acids, vinyl sulphonic acids and N-(3-hydroxyphenyl) methacrylamide. Alternatively, the dye can be functionalized to a copolymer to give the polymer of the current invention.

The antireflective polymer that is soluble in organic solvents can be synthesized by reacting any number of vinyl monomers containing at least one dye functionality described in Structure 1 and any number of vinyl monomers that do not contain a crosslinking functionality as described in Structure 2. Mixtures of different dye units from Structure 1 with different substituents and different units from Structure 2 can form a polymeric coating with the desired lithographic and physical properties. The substituents on each of the monomers can be chosen such that the polymer formed from these monomers is soluble in an organic solvent. Other unsaturated monomers can be added to the polymerization mixture that do not greatly effect the function of the antireflective coating. Alternatively, the dye can be functionalized to a copolymer to give the polymer of the current invention.

The process used for polymerization can be any of the ones known in the art for polymerizing vinyl polymers, such as, ionic or free radical polymerization. The polymer structure formed can be composed of alternate, block or random copolymers. The weight average molecular weight of the polymer ranges from about 500 to about 1,000,000, preferably from about 1,000 to about 100,000, and more preferably from about 3,000 to about 40,000.

The monomers can be polymerized in an organic solvent, where the solvent is the same as the casting solvent of the antireflective coating, preferably PGMEA, PGME or ethyl lactate.

The mole % of the dye containing monomer can range from about 5 to 100%, and the mole % of the non-crosslinking monomer or monomers can range from 0% to about 90% in the final polymer. Additionally, the polymer may contain unreacted precursors and/or monomers from the synthetic steps of the preparation of the polymer.

The coating composition comprises the polymer of the instant invention and a suitable solvent or mixtures of solvents. Other components may be added to enhance the performance of the coating, e.g. monomeric crosslinking agents, monomeric dyes, lower alcohols, additives to promote crosslinking, acid generators, thermally activated acid generators, acids, surface leveling agents, adhesion promoters, antifoaming agents etc. Examples of crosslinking agents include, but are not limited to, melamines, hydroxy alkyl amides, epoxy and epoxy amine resins, benzoquanamine resins, blocked isocyanates, glycolurils, dihydroxymethy benzenes, urea-formaldehyde resins and divinyl monomers. In a preferred embodiment the coating composition comprises the polymer of the instant invention, a crosslinking agent and solvent. Thermally activated acid generators and acids that can be used, but are not limited to, are 2,1,4 diazonaphthoquinone esters of multihydroxy phenolic compounds, alkyl and aryl sulfonic acids and esters, aromatic sulfonamides, alkyl and aryl phosphoric acids and esters, or thermal acid generators that are preferably activated at temperatures greater than 100°C. Monomeric dyes may also be added to the antireflective coating, examples of which are sudan orange, 2,4-dinitronaphthol, curcumin, coumarins and others.

The absorption of the antireflective coating can be optimized for a certain wavelength or range of wavelengths by the suitable choice of substituents on the dye functionality. Using substituents that are electron-withdrawing or electron donating generally shifts the absorption wavelength to longer or shorter wavelengths respectively. In addition, the solubility of the antireflective polymer in a particularly preferred solvent can be adjusted by the appropriate choice of substituents on the monomer.

The polymer of the antireflective coating composition is present in the range of about 1% to about 40% by total weight of solution. The exact weight used is dependent on the molecular weight of the polymer and the film thickness of the coating desired. Typical solvents, used as mixtures or alone, that can be used are propylene glycol monomethyl ether (PGME), propylene glycol monomethyl etheracetate (PGMEA), ethyl lactate, water, cyclopentanone, cyclohexanone, and gamma butyrolactone, but PGME, PGMEA and ethyl lactate or mixtures thereof are preferred. Solvents with a lower degree of toxicity, and good coating and solubility properties are generally preferred.

Since the antireflective film is coated on top of the substrate and is further subject to dry etching it is envisioned that the film is of sufficiently low metal ion level and purity that the properties of the semiconductor device are not adversely effected. Treatments such as passing a solution of the polymer through an ion exchange column or a combination of anion and cation exchange columns, filtration, and an extraction process can be used to reduce the concentration of metal ions and to reduce particles. Metal ion levels in the polymer below 50ppb each metal are preferred, below 10ppb are more preferred and below 1ppb are even more preferred.

The antireflective coating composition is coated on the substrate using techniques well known to those skilled in the art, such as dipping, spin coating or spraying. The film thickness of the antireflective coating typically ranges from about 0.1 micron to about 1micron. Thicker coatings, especially up to 10 microns, can also be used if necessary, especially for planarization of substrates with topography. The coating is further heated on a hot plate or convection oven to remove any residual solvent and to insolubilize the film.

Photoresists coated over the antireflective film can be any of the types used in the semiconductor industry.

There are two types of photoresist compositions, negative-working and positive-working. When negative-working photoresist compositions are exposed image-wise to radiation, the areas of the resist composition exposed to the radiation become less soluble to a developer solution (e.g. a cross-linking reaction occurs) while the unexposed areas of the photoresist coating remain relatively soluble to such a solution. Thus, treatment of an exposed negative-working resist with a developer causes removal of the non-exposed areas of the photoresist coating and the creation of a negative image in the coating. Thereby uncovering a desired portion of the underlying substrate surface on which the photoresist composition was deposited.

On the other hand, when positive-working photoresist compositions are exposed image-wise to radiation, those areas of the photoresist composition exposed to the radiation become more soluble to the developer solution (e.g. a rearrangement reaction occurs) while those areas not exposed remain relatively insoluble to the developer solution. Thus, treatment of an exposed positive-working photoresist with the developer causes removal of the exposed areas of the coating and the creation of a positive image in the photoresist coating. Again, a desired portion of the underlying surface is uncovered.

Positive working photoresist compositions are currently favored over negative working resists because the former generally have better resolution capabilities and pattern transfer characteristics. Photoresist resolution is defined as the smallest feature which the resist composition can transfer from the photomask to the substrate with a high degree of image edge acuity after exposure and development. In many manufacturing applications today, resist resolution on the order of less than one micron are necessary. In addition, it is almost always desirable that the developed photoresist wall profiles be near vertical relative to the substrate. Such demarcations between developed and undeveloped areas of the resist coating translate into accurate pattern transfer of the mask image onto the substrate. This becomes even more critical as the drive toward miniaturization reduces the critical dimensions on the devices.

Positive-acting photoresists comprising novolak resins and quinone-diazide compounds as photoactive compounds are well known in the art. Novolak resins are typically produced by condensing formaldehyde and one or more multi-substituted phenols, in the presence of an acid catalyst, such as oxalic acid. Photoactive compounds are generally obtained by reacting multihydroxyphenolic compounds with naphthoquinone diazide acids or their derivatives. The sensitivity of these types of resists typically ranges from about 300nm to 440nm.

Photoresists sensitive to short wavelengths, between about 180nm and about 300nm can also be used. These resists normally comprise polyhydroxystyrene or substituted polyhydroxystyrene derivatives, a photoactive compound, and optionally a solubility inhibitor. The following references exemplify the types of photoresists used and are incorporated herein by reference, US 4,491,628, US 5,069,997 and US 5,350,660.

The process of the instant invention further comprises coating a substrate with the novel antireflective coating composition and heating on a hotplate or convection oven at a sufficiently high temperature for sufficient length of time to remove the coating solvent in order to insolubilize the polymer to a sufficient extent so as not to be soluble in the coating solvent of the photoresist or in the aqueous alkaline developer. Various substrates known in the art may be used, such as those that are planar, have topography or have holes. The preferred range of temperature is from about 70°C to about 250°C, preferably from about 100°C to about 200°C. If the temperature is below 70°C then insufficient loss of solvent or insufficient degree of insolubilization takes place and at temperatures above 250°C the polymer may become chemically unstable. The exact temperature to be used is determined by the specific application. A film of a

photosensitive material is then coated on top of the antireflective coating and baked to substantially remove the photoresist solvent. The photoresist is imagewise exposed and developed in an aqueous developer to remove the treated resist. An optional heating step can be incorporated into the process prior to development and after exposure. The process of coating and imaging photoresists is well known to those skilled in the art and is optimized for the specific type of resist used. The patterned substrate is then be dry etched. The etching may be carried out in a suitable etch chamber to remove the exposed portions of the antireflective film, with the remaining photoresist acting as an etch mask. Optional heating steps may be included to optimize the etching process. Various etching techniques known in the art may be used.

An intermediate layer may be placed between the antireflective coating and the photoresist to prevent intermixing, and is envisioned as lying within the scope of this invention. The intermediate layer is an inert polymer cast from a solvent, where examples of the polymer are polysulfone and polyimides.

Another process that requires a bottom coat, such as the one of the present invention, is one where the photosensitive layer can be silylated to produce an etch resistant mask for etching the bottom coat. Such a process comprises forming a coating on a substrate with a bottom coat using the composition of the present invention, forming a photosensitive layer, imaging and developing the photosensitive layer, silylating this photosensitive layer with an appropriate silylating agent, and etching the bottom coat using the silylated photosensitive image as a mask. The concept of silylation is known to those skilled in the art and is described in the reference, Sebald et al, SPIE, Vol. 1262, pages 528-537, 1990. The photoresist to be silylated is designed, as known in the art, to be one capable of silylation. It has been found that the bottom coat of this invention is especially well-suited to this process since it has optimum etch properties.

The following specific examples will provide detailed illustrations of the methods of producing and utilizing compositions of the present invention. These examples are not intended, however, to limit or restrict the scope of the invention in any way and should not be construed as providing conditions, parameters or values which must be utilized exclusively in order to practice the present invention.

Examples

Example 1. Preparation of Polymer 1

To a 1-liter round bottom flask was added in sequence 360 ml of methanol, 60 ml of concentrated hydrochloric acid, and 50 grams of ethyl aminobenzoate. The solution was cooled to 10°C and 35 grams of iso-butyl nitrite was added to the flask while stirring. The diazotization reaction occurred immediately. After the addition of iso-butyl nitrite was completed, the solution was stored at 10°C and was ready for the coupling reaction.

To a 2-liter flask was added 65.5 grams of 2-(methacryloyloxy)ethyl acetoacetate(MEAA), 65 grams of pyridine, and 1.2 liters of methanol. The solution was cooled to 10°C and the above diazonium salt was added to the reactor. The coupling product formed immediately and precipitated out to give a suspension solution. After the addition of the diazonium salt was completed, the reactor was allowed to warm up to room temperature. The yellow solid, 4-ethyloxycarbonylphenylazo coupled product (ECP), was collected by filtration with a 90 % yield.

In a 1-liter flask, 100 grams of ECP were dissolved in tetrahydrofuran(THF). The solution was degassed by vigorously bubbling nitrogen through the solution for about 1 hour. Seventeen grams of methyl methacrylate(MMA) and a solution of 2,2'-azobisisobutyronotrile(AIBN) (1.4 grams) in THF were then injected into the solution and the polymerization mixture was further degassed for 30 minutes. The outlet needle was then removed and the sealed vessel allowed to stir at 65°C for 20 hours. This solution was then precipitated into 5 liters of 2-propanol. The polymer was collected as a yellow solid in 95 % yield. The UV-Visible spectrum of the polymer in ethyl lactate showed an absorption maximum(λmax) at 356 nm. Gel Permeation Chromatography spectrum showed the polymer has weight average molecular weight (Mw) of 32,769.

Example 2. Preparation of Polymer 2

To a 1-liter round bottom flask was added in sequence 360 ml of methanol, 60 ml of concentrated hydrochloric acid, and 45.5 grams of 4-aminoacetanilide. The solution was cooled to 10°C and 35 grams of iso-butyl nitrite was added to the flask under stirring. The diazotization reaction occurred immediately. After the addition of iso-butyl nitrite was completed, the solution was stored at 10°C in preparation for the coupling reaction.

To a 2-liter flask was added 65.5 grams of 2-(methacryloyloxy)ethyl acetoactate, 65 grams of pyridine, and 1.2 liters of methanol. The solution was cooled to 10°C and the above diazonium salt was added to the reactor. The coupling product formed immediately and precipitated out to give a suspension solution. After the addition of diazonium salt was completed, the reactor was allowed to warm up to room temperature. The yellow 4-acetoaminophenylazo coupled product (AAP) was collected by filtration with a 90 % yield.

In a 1-liter flask, 100 grams of the above AAP solid were dissolved in THF. The solution was degassed by vigorously bubbling nitrogen through the solution for about 1 hour. A solution of AIBN (1.4 grams) in THF was then injected into the solution and the polymerization mixture was further degassed for 30 minutes. The outlet needle was then removed and the sealed vessel was allowed to stir at 65°C for 20 hours. This solution was then precipitated into 5 liters of 2-propanol. The polymer was collected as a yellow solid with a 94 % yield. The UV-Visible spectrum of the polymer in ethyl lactate showed λmax at 389 nm. Gel Permeation Chromatography spectrum showed the polymer has weight average molecular weight (Mw) of 13,100.

Examples 3-8. Preparation of Polymers 3-8

Table 1 shows the polymers synthesized using the synthesis procedure described in Example 1 and gives the peak absorbance (λmax) in ethyl lactate(EL) and extinction coefficients (ε) for these polymers.

Table 1

Polymer #	AAP mole %	ECP mole%	MEAA mole%	MMA (mole%)	GPC (Mw)	λmax (nm)	ε (L/g.cm)
2	100				13,100	389	59
3		100			40,357	356	60
4	70			30	6,479	389	49
5		75	25		44,196	356	52
6		60		40	32,000	356	53
7		34	66		19,024	356	28
8		30	40	30	42,092	356	31

Example 9. Preparation of Polymer 9

To a 1-liter round bottom flask was added in sequence 200 ml of methanol, 40 ml of concentrated hydrochloric acid, and 25 grams of ethyl aminobenzoate. The solution was cooled to 10°C and 18 grams of iso-butyl nitrite was added to the flask under stirring. The diazotization reaction occurred immediately. After addition of iso-butyl nitrite was completed, the solution was stored at 10°C and ready for the coupling reaction.

To a 1-liter flask was added 32.0 grams of 2-(methacryloyloxy)ethyl acetoactate, 35 grams of pyridine, and 700 ml of methanol. The solution was cooled to 10°C and the above diazonium salt was added to the reactor. The coupling product formed immediately and precipitated out to give a suspension solution. After the addition of the diazonium salt was completed, the reactor was allowed to warm up to room temperature. The ECP solid was collected by filtration with a 92 % yield.

In a 1-liter flask, 50 grams of the above yellow solid was dissolved in THF. The solution was degassed by vigorously bubbling nitrogen through the solution for about 1 hour. 27 grams of methyl methacrylate, 29.6 grams of maleic anhydride, and a solution of AIBN (2.35 grams) in THF were then injected into the solution and the polymerization mixture was further degassed for 30 minutes. The outlet needle was then removed and the sealed vessel allowed stirring at 65°C for 20 hours. This solution was then precipitated into 5 liters of 2-propanol. The polymer was collected as a yellow solid in 96 % yield. The UV-Visible spectrum of the polymer in ethyl lactate showed λmax at 356 nm. GPC spectrum showed the polymer had a Mw of 8,044.

Examples 10-14

To a solution of 4.0 grams of each of the polymers specified in Table 2 and 96.0 grams of propyleneglycol monomethyl ether acetate(PGMEA) was added 0.48 grams of CYMEL® 303 and 0.04 grams of CYCAT® 600 (both available from CYTEC Industries, Inc.). The solution was spin-coated at 3000 rpm on to a 4-inch silicon wafer and baked on a hot plate at 180°C for 60 seconds. The coated wafers were then immersed in various resist casting solvents such as PGMEA and EL for 60 seconds and then spin-dried. The film thickness before and after immersion was measured by a NANOSPEC-AFT. The extent of interlayer mixing between the polymer and the solvent was determined by the changes of the polymer film thickness as listed in Table 2. It is clear

that the solubility of the polymer of the present invention in typical photoresist casting solvents is negligible.

Table 2

Example	Polymer	Solvent	T_1 (Å)	T_2 (Å)
10	1	PGMEA	748	747
11	1	EL	740	743
12	3	PGMEA	801	798
13	4	PGMEA	723	723
14	5	PGMEA	776	769

where,

T1: polymer film thickness before solvent immersion

T2: polymer film thickness after solvent immersion

Example 15

The polymer solutions formulated in Examples 10 and 12-14 were spin-coated on to 4-inch silicon wafers and baked on a hot plate at 180°C for 60 seconds to give a thickness of about 850Å. The wafers were then coated with AZ® 7908 photoresist (available from Clariant Corporation, 70 Meister Ave., Somerville, NJ 08876) and baked at 90°C for 90 seconds to give a thickness of 0.974µm. A 4-inch wafer coated with AZ® 7908 photoresist at 0.974µm and baked at 90°C for 70 seconds was used as the reference.

These wafers were imagewise exposed with a NIKON® 0.54 NA i-line stepper with a range of exposures. The exposed wafers were baked at 110°C for 60 seconds and puddle developed with AZ® 300 MIF Developer (available from Clariant Corporation, 70 Meister Ave., Somerville, NJ 08876) for 35 seconds. The resist pattern generated on these wafers were evaluated by a Hitachi S-4000 field emission scanning electron microscope. Table 3 shows the comparison of lithographic performance of AZ® 7908 photoresist with and without the bottom antireflective coatings of the present invention. The bottom polymer coatings of the present invention clearly improve the resolution and effectively eliminate standing waves caused by wafer substrate reflection, without sacrificing photosensitivity.

Table 3

Bottom Coating	DTP (mj/cm²)	Resolution (µm)	Standing Wave
Example 10	175	0.28	Eliminated
Example 12	180	0.28	Eliminated
Example 13	175	0.30	Eliminated
Example 14	175	0.30	Eliminated
None	170	0.38	Severe

where, DTP is dose to print

Example 16

The polymer solutions formulated in Examples 10, 13, and 14 were spin-coated on to 4-inch silicon wafers and baked on a hot plate at 180°C for 60 seconds to give a thickness of about 850Å. The wafers were then coated with AZ® 7908 photoresist (available from Clariant Corporation, 70 Meister Ave., Somerville, NJ 08876) and baked at 90°C for 90 seconds to give a resist thickness from 0.75µm to 1.10µm. These wafers were imagewise exposed with a NIKON® 0.54 NA i-line stepper, then baked at 110°C for 60 seconds and puddle developed with AZ® 300 MIF Developer for 35 seconds. The minimum dose required to clear the film was plotted as a function of resist thickness, a sinusoidal curve thus obtained is called the swing curve. The swing ratio of a photoresist is closely related to the linewidth variation of the photoresist pattern over a highly reflective substrate or topography commonly encountered in a semiconductor device manufacturing. The lower the swing ratio, the better the linewidth control over reflective substrate or topography. The swing ratio was calculated by the equation:

$$\text{Swing Ratio} = (E_{max} - E_{min})/(E_{max} + E_{min})$$

where,

Emax and Emin corresponding to the dose-to-clear of a resist thickness at the maximum and minimum on a swing curve. Swing curves were generated by plotting the dose required to clear a resist film after development as a function of the resist thickness.

$$\%\ \text{Swing Reduction} = \frac{(\text{Swing Ratio on silicon} - \text{Swing Ratio on polymer})}{\text{Swing Ratio on silicon}}$$

where, Swing Ratio on silicon and Swing Ratio on polymer correspond to the swing ratio of photoresist coated on silicon wafer and on polymer bottom coating respectively.

The %Swing Reduction of AZ® 7908 photoresist over the polymer coatings of the present invention are listed in Table 4.

Table 4

Bottom Coating	% Swing Reduction
None	0
Example 10	88
Example 13	75
Example 14	85

It is clear that the polymer coatings of the present invention can effectively reduce the swing ratios of the photoresist.

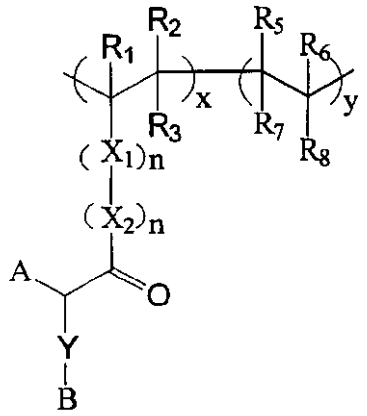
Example 17

A silicon wafer was coated with a solution of 30 weight % Polymer 8 with a Mw of about 17,000 in ethyl lactate. The silicon wafer was heated for 60 seconds at 170°C to give a coating of 4 microns. The wafer was then coated with AZ® CP365 photoresist (available from Clariant Corporation) and baked at 110°C for 60 seconds. The substrate was imaged using an I-line stepper with varying exposure energies ranging from 80 $mJcm^{-2}$ to 150 $mJcm^{-2}$. The latent image was developed with AZ® 300 MIF developer for 60 seconds using the stream/puddle mode. Silylation was done using a 2 weight% Tegomer solution a siloxane polymer (available from Shin-Etsu Corporation) hexanol for 2 minutes. The pattern was transferred to the substrate using reactive ion etching with oxygen and argon gases. Secondary electron microscope images showed a complete image transfer.

Claims

1. A coating composition for use in photolithography, comprising

a) a polymer having a structure,



where,

R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

R_5-R_8 do not have a crosslinking group and are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, hydroxyalkyl, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, hydroxy (C_1-C_{10}) alkyl, (C_1-C_{10})alkyl$OCOCH_2COCH_3$, or R_7 and R_8 combine to form a cyclic group,

X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,

X_2 is S, S(C_1-C_{10}) alkyl , O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),

n is independently 0-2,

A is an electronwithdrawing group,

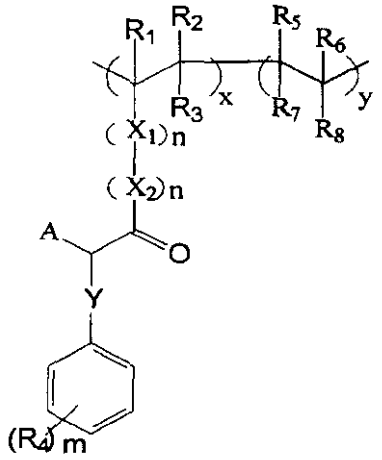
Y is a conjugated moiety e.g. N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

$x > 0$, and $y \geq 0$, and

B is selected from a 5-10 membered aromatic group, polyaromatic group or a heterocyclic aromatic group; and,

b) a suitable solvent.

2. A coating composition according to claim 1, where the polymer has a structure,



where,

R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

R_5-R_8 do not have a crosslinking group and are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, hyroxyalkyl, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, hydroxy (C_1-C_{10}) alkyl, (C_1-C_{10})alkylOCOCH$_2$COCH$_3$, or R_7 and R_8 combine to form a cyclic group,

X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,

X_2 is S, S(C_1-C_{10}) alkyl , O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),

n is independently 0-2,

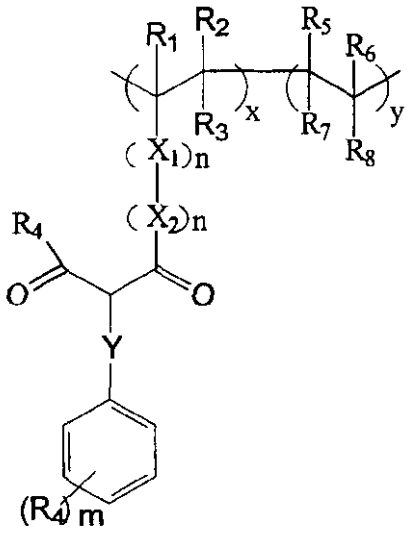
A is an electronwithdrawing group,

R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl or SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl,

Y is a conjugated moiety N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

$m = 1\text{-}5$, $x > 0$, and $y \geq 0$.

3. The coating composition according to claim 1, wherein the polymer has a structure,



where,

R_1-R_3 are independently H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

R_5-R_8 do not have a crosslinking group and are independently H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2, where Z is H or (C_1-C_{10}) alkyl, hydroxy (C_1-C_{10}) alkyl, (C_1-C_{10})alkyl$OCOCH_2COCH_3$, or R_7 and R_8 combine to form a cyclic group,

X_1 is C=O, OCO, CONH, O, aryl, (C_1-C_{10}) alkyl, cyclohexyl, pyridine or pyrollidone,

X_2 is S, S(C_1-C_{10}) alkyl , O, O(C_1-C_{10}) alkyl, NH, N(C_1-C_{10}) alkyl, alkyl, or hydroxyalkyl(C_1-C_{10}),

n is independently 0-2,

R_4 is H, (C_1-C_{10}) alkyl, (C_1-C_{10}) alkoxy, nitro, halide, cyano, aryl, alkylaryl, alkenyl, dicyanovinyl, SO_2CF_3, COOZ, SO_3Z, COZ, OZ, NZ_2, SZ, SO_2Z, NHCOZ, SO_2NZ_2,where Z is H or (C_1-C_{10}) alkyl,

Y is a conjugated moiety N=N, CW=CW, CW=N, or N=CW, where W is H, (C_1-C_{10}) alkyl or (C_1-C_{10}) alkoxy,

m = 1-5, $x > 0$, and $y \geq 0$.

4. The coating composition according to claim 1, wherein the solvent comprises a mixture of organic solvents.

5. The coating composition according to claim 1, wherein the solvent is selected from a group consisting of propylene glycol monomethyl ether, propylene glycol monomethyl etheracetate, ethyl lactate, heptanone, cyclopentanone, cyclohexanone, gamma butyrolactone and, water.

6. The coating composition according to claim 1, wherein Y is N=N.

7. The coating composition of claim 1, wherein y=0.

8. The coating composition according to claim 1, wherein the polymer further comprises one or more vinyl monomers that are nonabsorbing and noncrosslinking.

9. The coating composition according to claim 1, wherein R_8 is selected from hydroxyl, alkyl hydroxyl, carboxylic acid or its esters, sulfonic acid or its esters, phenolics, ethers, acrylamides and N-(3-Hydroxyphenylmethacrylamide).

10. The coating composition according to claim 1, wherein R_8 and R_7 are combined to form anhydride, pyridine, maleimde, or pyrollidone.

11. The coating composition according to claim 1, wherein the polymer further comprises at least one unit derived from a hydrophilic vinyl monomer or a vinyl monomer capable of becoming hydrophilic.

12. The aqueous antireflective composition according to claim 11, wherein the hydrophilic group is selected from a group consisting of $O(CH_2)_2$-O-(CH_2)-OH, $O(CH_2)_2$-OH, $(CH_2)_n$-OH (where n=1-4), $COO(C_1$-$C_4)$alkyl, COOX, and SO_3X (where X is H, alkali metal, ammonium, alkyl ammonium).

13. The coating composition according to claim 1, further comprising a dye.

14. The coating composition according to claim 1, further comprising a crosslinking agent.

15. The coating composition according to claim 14, further comprising an acid.

16. The coating composition according to claim 14, further comprising an acid generator.

17. The coating composition according to claim 15, wherein the acid generator is a thermally activated acid generator.

18. The coating composition according to claim 1, wherein the polymer has a weight average molecular weight in the range of about 500 to about 1,000,000.

19. The coating composition according to claim 1, wherein the metal ion level is less than 50ppb each metal ion.

20. The process of forming an image on a substrate comprising the steps of:

a) providing a coating of the coating composition of claim 1 on the substrate;
b) providing a coating of a photosensitive material;
c) imagewise exposing the photosensitive material;
d) developing the imagewise exposed photosensitive material; and
e) dry etching the coating composition.

21. The process of claim 20, wherein the photoresist solution comprises a novolak resin, a photosensitive compound and a solvent.

22. The process of claim 20, wherein the photoresist solution comprises a substituted polyhydroxystyrene, a photoactive compound and a solvent.

23. The process of claim 20, wherein the photoresist solution comprises polyhydroxystyrene, a photoactive compound, a dissolution inhibitor and a solvent.

24. The process of claim 20, wherein the heating temperature for the antireflective coating ranges from about 70°C to about 250°C.

25. The process of claim 20, wherein the film thickness of the antireflective coating ranges from 0.1 micron to 10 microns.

26. The process of claim 20, wherein the developer is an aqueous solution of metal ion free alkaline hydroxide.

27. The process of claim 20, wherein the photosensitive material is capable of being silylated.

28. The process of claim 28, where after developing and prior to dry etching, reacting the photosensitive material with a silylating material.

INTERNATIONAL SEARCH REPORT

Inte onal Application No
PCT/EP 00/07228

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 G03F7/09 C08F20/36 C09B69/10

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 G03F C08F C09B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	KERBER, NUYKEN, STEINHAUSEN: "Synthese und characterisierung von copolymeren aus azo-initiatoren und styrol" MAKROMOLEKULARE CHEMIE, MACROMOLECULAR CHEMISTRY AND PHYSICS., vol. 177, 1975, pages 1357-1371, XP002151443 HUTHIG UND WEPF VERLAG, BASEL., CH ISSN: 0025-116X the whole document --- -/--	1

[X] Further documents are listed in the continuation of box C. [ ] Patent family members are listed in annex.

° Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
1 November 2000	14. 12. 2000

Name and mailing address of the ISA	Authorized officer
European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Schueler, D

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Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Inte ional Application No
PCT/EP 00/07228

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication,where appropriate, of the relevant passages	Relevant to claim No.
A	CALGARI, SELLI, BELLOBONO: "photochemical grafting of acrylated azo dyes onto polymeric surfaces" JOURNAL OF APPLIED POLYMER SCIENCE., vol. 27, no. 2, 1982, pages 527-533, XP002151444 JOHN WILEY AND SONS INC. NEW YORK., US ISSN: 0021-8995 the whole document	1

Form PCT/ISA/210 (continuation of second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

...ernational application No.
PCT/EP 00/07228

Box I Observations where certain claims were found unsearchable (Continuation of item 1 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☒ Claims Nos.:
because they relate to parts of the International Application that do not comply with the prescribed requirements to such *an extent that no meaningful International Search can be carried out, specifically:*

see FURTHER INFORMATION sheet PCT/ISA/210

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box II Observations where unity of invention is lacking (Continuation of item 2 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is *restricted to the invention first mentioned in the claims; it is covered by claims Nos.:*

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Present claim 1 relate to a compound/product defined (inter alia)

by reference to the following parameter(s):
P1: "suitable solvent"
The use of this parameter in the present context is considered to lead to a lack of clarity within the meaning of Article 6 PCT. It is impossible to compare the parameter the applicant has chosen to employ with what is set out in the prior art. The lack of clarity is such as to render a meaningful complete search impossible. Consequently, the search has been restricted to the list of solvents as defined in claim 5.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

[19]中华人民共和国国家知识产权局

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[12]发明专利申请公开说明书

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权利要求书6页 说明书19页 附图页数0页

[54]发明名称 用于光致抗蚀剂组合物的抗反射涂料

[57]摘要

本发明涉及一种新型抗反射涂料组合物及其在光刻中应用的方法。该抗反射涂料溶液包含一种新型聚合物和一种有机溶剂或溶剂的混合物,其中所述新型聚合物包含含有可吸收约180nm到约450nm的染料的单元且不含交联基团。

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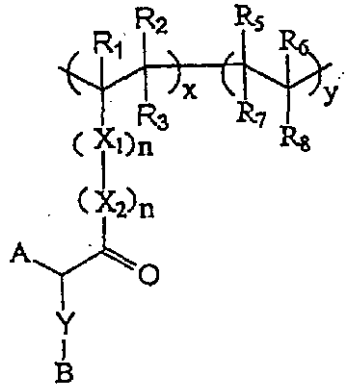
权 利 要 求 书

1. 一种用于光刻的涂料组合物，包含:

a) 具有下式结构的聚合物，



其中，

R_1-R_3 独立地为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

R_5-R_8 不含交联基团并独立地为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、羟烷基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基、SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基、羟(C_1-C_{10})烷基、(C_1-C_{10})烷基 $OCOCH_2COCH_3$，或 R_7 和 R_8 结合形成环状基团，

X_1 为 C=O、OCO、CONH、O、芳基、(C_1-C_{10})烷基、环己基、吡啶或 pyrollidone，

X_2 为 S、S(C_1-C_{10})烷基、O、O(C_1-C_{10})烷基、NH、N(C_1-C_{10})烷基、烷基、或羟烷基(C_1-C_{10})，

n 独立为 0 - 2，

A 为吸电子基团，

Y 为共轭部分，例如 N = N、CW = CW、CW = N、或 N = CW，其中 W 为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

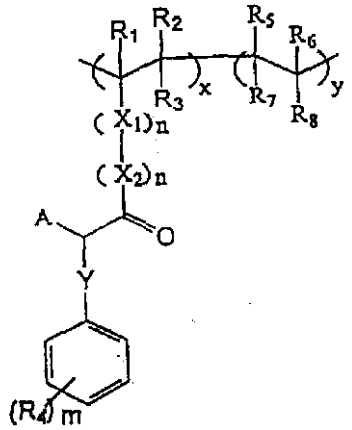
$x>0$，且 $y\geq 0$，且

B 选自 5 - 10 元芳族基团、多芳族基团或杂环芳族基团；和

b) 一种合适的溶剂。

02.01.31

2. 根据权利要求 1 的涂料组合物，其中聚合物具有下式结构:



其中，

R_1-R_3 独立地为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

R_5-R_8 不含交联基团并独立地为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、羟烷基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基、SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基、羟(C_1-C_{10})烷基、(C_1-C_{10})烷基 $OCOCH_2COCH_3$，或 R_7 和 R_8 结合形成环状基团，

X_1 为 C=O、OCO、CONH、O、芳基、(C_1-C_{10})烷基、环己基、吡啶或 pyrollidone，

X_2 为 S、S(C_1-C_{10})烷基、O、O(C_1-C_{10})烷基、NH、N(C_1-C_{10})烷基、烷基、或羟烷基(C_1-C_{10})，

n 独立为 0 - 2，

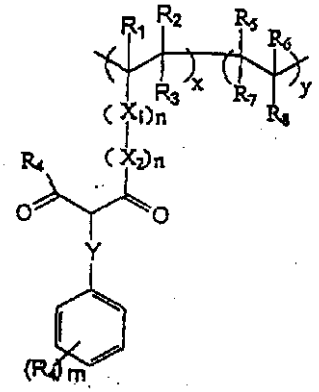
A 为吸电子基团，

R_4 为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基或 SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基，

Y 为共轭部分，例如 N = N、CW = CW、CW = N、或 N = CW，其中 W 为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

m=1 - 5，　x>0，且 y ≥ 0。

3. 根据权利要求 1 的涂料组合物，其中聚合物具有下式结构:



其中，

R_1-R_3 独立地为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

R_5-R_8 不含交联基团并独立地为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、羟烷基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基、SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基、羟(C_1-C_{10})烷基、(C_1-C_{10})烷基 $OCOCH_2COCH_3$，或 R_7 和 R_8 结合形成环状基团，

X_1 为 C=O、OCO、CONH、O、芳基、(C_1-C_{10})烷基、环己基、吡啶或 pyrollidone，

X_2 为 S、S(C_1-C_{10})烷基、O、O(C_1-C_{10})烷基、NH、N(C_1-C_{10})烷基、烷基、或羟烷基(C_1-C_{10})，

n 独立为 0－2，

R_4 为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基或 SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基，

Y 为共轭部分，例如 N＝N、CW＝CW、CW＝N、或 N＝CW，其中 W 为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

m=1－5，　x>0，且 y≥0。

4. 根据权利要求 1 的涂料组合物，其中所述溶剂包括有机溶剂的混合物。

5. 根据权利要求 1 的涂料组合物，其中所述溶剂选自丙二醇一单醚、丙二醇单甲醚乙酸酯、乳酸乙酯、辛酮、环戊酮、环己酮、γ-丁内酯，和水。

6. 权利要求 1 的涂料组合物，其中 Y 为 N=N.

7. 权利要求 1 的涂料组合物，其中 y=0.

8. 根据权利要求 1 的涂料组合物，其中聚合物进一步包含一种或多种不吸收且不交联的乙烯基单体.

9. 根据权利要求 1 的涂料组合物，其中 R_8 选自羟基、烷羟基、羧酸及其酯、磺酸及其酯、酚类、醚类、丙烯酰胺和 N-(3-羟苯基甲基丙烯酰胺).

10. 根据权利要求 1 的涂料组合物，其中 R_8 和 R_7 结合起来形成酸酐、吡啶、马来酰亚胺，或 pyrollidone.

11. 根据权利要求 1 的涂料组合物，其中聚合物进一步包含至少一种衍生自亲水乙烯基单体或可变得亲水的乙烯基单体的单元.

12. 根据权利要求 11 的水性抗反射组合物，其中亲水基团选自 $O(CH_2)_2$-O-(CH_2)-OH、$O(CH_2)_2$-OH、$(CH_2)_n$-OH(其中 n=0-4)，$COO(C_1$-$C_4)$ 烷基、COOX 和 SO_3X（其中 X 为 H、碱金属、铵、烷基铵）。

13. 根据权利要求 1 的涂料组合物，进一步包含染料。

14. 根据权利要求 1 的涂料组合物，进一步包含交联剂。

15. 根据权利要求 14 的涂料组合物，进一步包含一种酸。

16. 根据权利要求 14 的涂料组合物，进一步包含一种生酸剂。

17. 根据权利要求 15 的涂料组合物，其中所述生酸剂为热活化生酸剂。

18. 根据权利要求 1 的涂料组合物，其中所述聚合物具有范围为约 500 到约 1000000 的重均分子量。

19. 根据权利要求 1 的涂料组合物，其中每种金属离子的金属离子水平低于 50ppb。

20. 一种在基材上形成图像的方法，包括:

a) 在基材上提供权利要求 1 的涂料组合物的涂层;

b) 提供光敏材料的涂层;

c) 对光敏材料进行图样曝光;

d) 对图样曝光的光敏材料进行显影; 和

e) 对涂料组合物进行干蚀刻。

21. 权利要求 20 的方法，其中光致抗蚀剂溶液包含酚醛清漆树脂、光敏化合物和溶剂。

22. 权利要求 20 的方法，其中光致抗蚀剂溶液包含取代的聚羟基苯乙烯、光活性化合物和溶剂。

23. 权利要求 20 的方法，其中光致抗蚀剂溶液包含聚羟基苯乙烯、光活性化合物、溶解抑制剂和溶剂。

24. 权利要求 20 的方法，其中加热抗反射涂层的温度范围为约 70℃到约 250℃。

25. 权利要求 20 的方法，其中抗反射膜涂层的厚度范围为 0.1 微米到 10 微米。

26. 权利要求 20 的方法，其中显影剂是无金属离子的碱性氢氧化物的水溶液。

27. 权利要求 20 的方法，其中光敏材料具有被甲硅烷基化的能力。

28. 权利要求 28 的方法，其中在显影之后、干刻蚀之前，将光敏材料与甲硅烷基化材料反应。

说　明　书

用于光致抗蚀剂组合物的抗反射涂料

发明背景

本发明涉及新型抗反射涂料组合物及其在反射基材和光敏涂层间形成薄层的用途。这些组合物在用光刻技术制造半导体设备中尤为有用。而且，该新型聚合物可用作光致抗蚀剂组成中的吸收聚合物。

光致抗蚀剂组合物被用于制造微型化电气组件的微刻工艺中，例如计算机芯片和集成电路的制造中。通常，在这些工艺中，首先将光致抗蚀剂组合物的薄膜涂层涂覆在基材上，例如用于制造集成电路的硅晶片上。而后烘焙涂覆的基材蒸发光致抗蚀剂组合物中的所有溶剂并将涂层固定在基材上。而后对基材的烘焙的涂覆表面进行图样（image-wise）的辐射曝光。

这种辐射曝光导致涂覆表面的曝光区域的化学变化。可见光、紫外(UV)光、电子束和 X－射线辐射能是当今在微刻工艺中普遍使用的辐射种类。在图样曝光之后，涂覆的基材用显影剂溶液进行处理，溶解和去除辐射曝光或未曝光区域的光致抗蚀剂。

半导体设备的微型化的趋势导致多级尖端体系的使用，以克服与微型化相关的困难。在光刻中，高吸收抗反射涂层的使用是一种减小由高反射基材背反射造成的问题的较为简单的方法。背反射的两个有害作用是薄膜干涉和反射刻痕(reflective notching)。薄膜干涉由于抗蚀膜中总光强的变化使抗蚀剂的厚度改变从而导致临界线宽尺寸的改变。线宽的变化与摆动比(swing ratio)(S)成比例，因此为更好控制线宽必须最小化 S。摆动比定义为：

$$S=4(R_1R_2)^{1/2}e^{-\alpha D}$$

其中，

R_1 为在抗蚀剂/空气或抗蚀剂/顶涂层界面的反射率，

R_2 为在抗蚀剂/基材界面的反射率，

α为抗蚀剂的光学吸收系数，和D为膜厚。

抗反射涂层的功能为对用于对光致抗蚀剂进行曝光的辐射的吸收，即，减小 R_2，从而减小摆动比。当光致抗蚀剂涂覆于含有起伏特征的基材时反射刻痕变得严重，该起伏特征使光在光致抗蚀剂膜中散射，导致线宽的变化，在极端情况下形成抗蚀剂全部损失的区域。

过去，曾使用染料光致抗蚀剂解决反射问题。然而，公知染料抗蚀剂仅减小反射而不能完全消除它。此外，染料抗蚀剂可能导致光致抗蚀剂的刻蚀性能的降低，还有染料可能升华以及染料与抗蚀膜不相容的问题。当需要进一步减小或消除摆动比时，应在涂覆光致抗蚀剂和曝光前在基材上涂覆抗反射涂层。该抗蚀剂进行图样曝光并显影。曝光区域的抗反射涂层随后通常在氧基等离子体中被蚀刻，这样便将刻蚀图案转印到基材上。对抗反射膜的蚀刻速率应相对较高，使得在蚀刻过程中抗反射膜被蚀刻而没有过多的抗蚀膜的损失。

含有吸收光的染料和提供涂层性质的聚合物的抗反射涂层是公知的。然而，在加热过程中可能的升华和染料扩散至光致抗蚀剂层中使得此种类型的抗反射组合物不令人满意。

聚合物有机抗反射涂料是公知的，并被记载在 EP 583,205 和 US 5,525,457 中，在此将其引入本文作为参考。然而，这些抗反射膜用有机溶剂流延（cast from），例如环已酮和环戊酮。使用有机溶剂的潜在危险导致本发明的抗反射涂层组合物的开发，其中抗反射涂层的固体组成溶解并流延于较低毒性的溶剂中。与其它溶剂相比具有低毒性的半导体工业公知的优选的溶剂是丙二醇单甲醚乙酸酯(PGMEA)，丙二醇一甲醚(PGME)，和乳酸乙酯。

在另一实施方案中，通过选择亲电取代基和共聚单体，本发明的聚合物可由水流延。水基涂料不仅优选而且由于其易于处理提供在半导体工业中的显著优点。

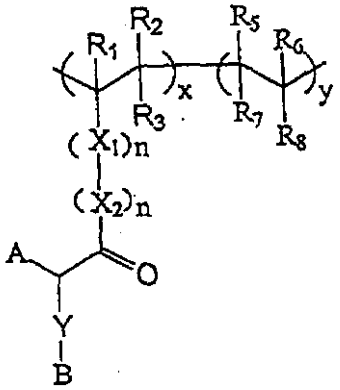
公开于 US5,652,297 和 US5,652,317 的聚合物涂料可溶于优选的溶剂，但与本发明相比包含不同的发色侧基。公开于 US5,733,714 的发色基团与本发明相似，但 US5,733,714 中含有交联基团。现在出乎

意料地发现，含有与 US714 中公开的发色侧基相似的基团的均聚物，和由含有相同发色侧基的单体与不含交联基团的共聚单体合成的共聚物，均可有效地用于光致抗蚀剂的底涂层或用作光致抗蚀剂的添加剂。在一些例子中已经发现，优选含有一种不含具有交联基团的共聚单体的聚合物，因为交联基团可能导致溶液或涂层的不稳定或不溶。

本发明的聚合物含有特定的染料官能团，而且，该聚合物可以是不含交联基团的特定种类的单体的均聚物或共聚物。由本发明的抗反射涂料形成良好的涂层，并且在抗反射涂层和光致抗蚀膜之间没有出现混合。由该聚合物形成的涂层当用作光致抗蚀剂的底涂层时还具有优异的干蚀刻性能，可使图像很好地从抗蚀膜转印到基材上，并具有优异的吸收性能防止反射刻痕和线宽变化。

本发明简述

本发明涉及一种新型抗反射涂料组合物及其在光刻中应用的方法。该抗反射涂料组合物的聚合物含有至少一个含染料而不含交联基团的单元。该染料官能团是一种能强烈吸收从约 180nm（纳米）到约 450nm 辐射的官能团。该抗反射涂料组合物含有一种溶剂和一种如下结构的聚合物：



其中，

R_1-R_3 独立地为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

R_5-R_8 不含交联基团并独立地为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、羟烷基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基、SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基、羟(C_1-C_{10})烷基、(C_1-C_{10})烷基 $OCOCH_2COCH_3$，或 R_7 和

R_8结合形成环状基团，

X_1为 C=O、OCO、CONH、O、芳基、(C_1-C_{10})烷基、环己基、吡啶或 pyrollidone，

X_2为 S、S(C_1-C_{10})烷基、O、O(C_1-C_{10})烷基、NH、N(C_1-C_{10})烷基、烷基、或羟烷基(C_1-C_{10})，

n 独立为 0－2，

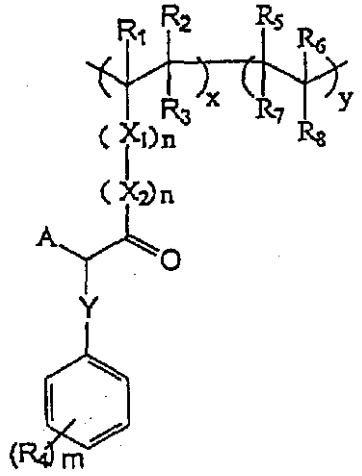
A 为吸电子基团，

Y 为共轭部分，例如 N＝N、CW＝CW、CW＝N、或 N＝CW，其中 W 为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

x>0，且 y≥0，且

B 选自 5－10 元芳族基团、多芳族基团或杂环芳族基团。

优选该聚合物具有如下结构：



其中，

R_1-R_3独立地为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

R_5-R_8不含交联基团并独立地为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、羟烷基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基、SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基、羟(C_1-C_{10})烷基、(C_1-C_{10})烷基 $OCOCH_2COCH_3$，或 R_7和 R_8结合形成环状基团，

X_1为 C=O、OCO、CONH、O、芳基、(C_1-C_{10})烷基、环己基、吡啶或 pyrollidone，

X_2为 S、S(C_1-C_{10})烷基、O、O(C_1-C_{10})烷基、NH、N(C_1-C_{10})烷基、烷

基、或羟烷基(C_1-C_{10})，

n 独立为 0 - 2，

A 为吸电子基团，

R_4 为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基或 SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基，

Y 为共轭部分，例如 N = N、CW = CW、CW = N、或 N = CW，其中 W 为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

m=1 - 5， x>0，且 y≥0。

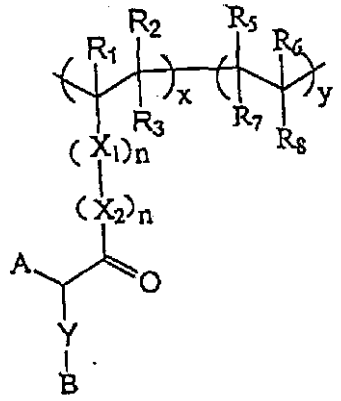
本发明还包含一种在基材上形成图像的方法。所述基材上涂布有本发明的抗反射涂料，并加热除去所有残余溶剂并使涂层不溶解。而后在抗反射涂层的上面形成光致抗蚀剂溶液的薄膜，进一步加热基本上除去光致抗蚀剂溶剂。该光致抗蚀膜通过掩膜用约 180nm 到约 450nm 的紫外光辐射进行图样曝光，并在碱性显影剂的水溶液中加工得到光刻蚀图像。该基材可在显影步骤之前或之后加热从而得到更高质量的图像。曝光的抗反射膜可随后被干蚀刻，通常在氧基等离子体中，用光刻蚀图像作为蚀刻掩膜。在本发明的另一实施方案中，在显影步骤之后、蚀刻步骤之前引入甲硅烷化步骤。

发明详述

本发明的涂料组合物包含一种聚合物，该聚合物可以是由一种含特殊结构的染料单体得到的均聚物，或由该染料单体与一种不含交联基团的单体反应得到的共聚物，并且，由此得到的聚合物对波长范围 180nm 到约 450nm 的紫外光有强烈吸收。本发明进一步提供一种在基材上涂布和烘焙抗反射涂层、以及在该抗反射涂层上涂覆和影印光致抗蚀膜、和随后对抗反射涂层进行蚀刻的方法。

本发明的聚合物通过由至少一种含染料官能团的乙烯基单体反应得到均聚物或其与至少另一种不含交联基团的乙烯基单体反应形成共聚物而得到。该染料官能团是一种对约 180nm 到约 450nm 的辐射有强烈吸收的官能团。可以使用的优选的染料单体单元的类型用下面的结

构定义:



结构 1

其中,

R_1-R_3 独立地为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基,

R_5-R_8 不含交联基团并独立地为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、羟烷基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基、SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2,其中 Z 为 H 或(C_1-C_{10})烷基、羟(C_1-C_{10})烷基、(C_1-C_{10})烷基 $OCOCH_2COCH_3$,或 R_7 和 R_8 结合形成环状基团,

X_1 为 C=O、OCO、CONH、O、芳基、(C_1-C_{10})烷基、环己基、吡啶或 pyrollidone,

X_2 为 S、S(C_1-C_{10})烷基、O、O(C_1-C_{10})烷基、NH、N(C_1-C_{10})烷基、烷基、或羟烷基(C_1-C_{10}),

n 独立为 0 - 2,

A 为吸电子基团,

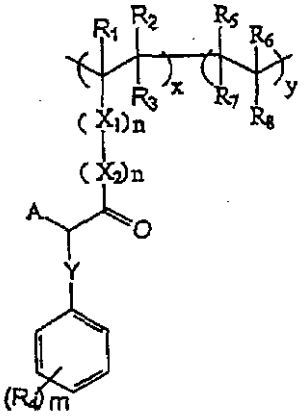
Y 为共轭部分,例如 N = N、CW = CW、CW = N、或 N = CW,其中 W 为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基,

x>0,且 y≥0,且

B 选自 5 - 10 元芳族基团、多芳族基团或杂环芳族基团.

所述发色侧基 B 为芳族部分,例如取代或未取代的 5 - 10 芳族烃环、取代或未取代的多核芳族烃环,例如苯基、萘基或蒽基、或取代或未取代的杂环芳族基团,例如吡啶、吲哚、pyrazore、噻吩等.

优选该聚合物具有如下结构:



其中，

R_1-R_3 独立地为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

R_5-R_8 不含交联基团并独立地为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、羟烷基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基、SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基、羟(C_1-C_{10})烷基、(C_1-C_{10})烷基 $OCOCH_2COCH_3$，或 R_7 和 R_8 结合形成环状基团，

X_1 为 C=O、OCO、CONH、O、芳基、(C_1-C_{10})烷基、环己基、吡啶或 pyrollidone，

X_2 为 S、S(C_1-C_{10})烷基、O、O(C_1-C_{10})烷基、NH、N(C_1-C_{10})烷基、烷基、或羟烷基(C_1-C_{10})，

n 独立为 0 - 2，

A 为吸电子基团，

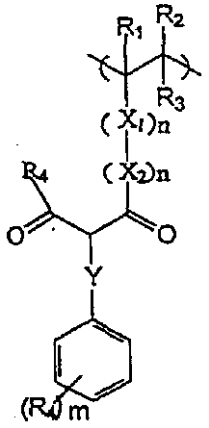
R_4 为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基或 SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基，

Y 为共轭部分，例如 N = N、CW = CW、CW = N、或 N = CW，其中 W 为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

m=1 - 5，　x>0，且 y ≥ 0。

所述基团 A 为吸电子基团，并优选为 COR_4、CN 或 CZ。

该染料单元更优选的结构为：



其中，

R_1-R_3 独立地为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，

X_1 为 C=O、OCO、CONH、O、芳基、(C_1-C_{10})烷基、环己基、吡啶或 pyrollidone，

X_2 为 S、S(C_1-C_{10})烷基、O、O(C_1-C_{10})烷基、NH、N(C_1-C_{10})烷基、烷基、或羟烷基(C_1-C_{10})，

n = 0 - 2，

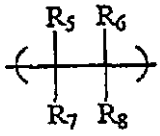
A 为吸电子基团，

R_4 为 H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基或 SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中 Z 为 H 或(C_1-C_{10})烷基，

Y 为共轭部分，例如 N = N、CW = CW、CW = N、或 N = CW，其中 W 为 H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，和

m=1 - 5。

在本发明的一个优选的实施方案中聚合物用作被等离子体蚀刻的底涂层，共聚物是优选的，其中该共聚物具有至少一个如结构 1 的染料单元和一个下面结构 2 的单元：

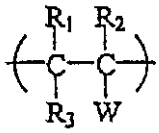


结构2

其中，

R_5-R_8不含交联基团并独立地为H、(C_1-C_{10})烷基、(C_1-C_{10})烷氧基、羟烷基、硝基、卤素、氰基、芳基、烷芳基、亚烷基、二氰基乙烯基、SO_2CF_3、COOZ、SO_3Z、COZ、OZ、NZ_2、SZ、SO_2Z、NHCOZ、SO_2NZ_2，其中Z为H或(C_1-C_{10})烷基、羟(C_1-C_{10})烷基、(C_1-C_{10})烷基$OCOCH_2COCH_3$，或R_7和R_8结合形成环状基团，例如酸酐、吡啶或pyrollidone。

在另一实施方案中，在聚合物中与含染料官能团的单元一起，存在一种促进共聚物水溶性的亲水单体单元，并且该亲水单体可由下面结构表示：



R_1-R_3独立地为H、(C_1-C_{10})烷基或(C_1-C_{10})烷氧基，且W为亲水基团。

亲水基团W的例子为，但不限于：$O(CH_2)_2$-O-(CH_2)-OH、$O(CH_2)_2$-OH、$(CH_2)_n$-OH(其中n=0-4)、COO(C_1-C_4)烷基、COOX和SO_3X（其中X为H、碱金属、铵、烷基铵）。其它也可用于形成该聚合物的亲水乙烯基单体有马来酸酐、马来酰亚胺、乙烯基吡啶和pyrollidone。

水溶性抗反射聚合物可通过任何数量的结构1所描述的含有至少一个染料官能团的乙烯基单体，任何数量的不含交联官能团的乙烯基单体（结构2）和/或任何数量的亲水乙烯基单体反应而合成。可以聚合不同的染料单体、不同的不含交联基团的单体和不同的亲水单体的混合物而赋予抗反射涂层最佳的所需刻蚀性能和物理性能。其它不破坏该聚合物功能的不饱和单体也可加入到聚合混合物中。这些不饱和单体的例子有马来酸酐、乙酸乙烯酯、乙烯基醚、乙烯基丙烯酰胺、乙烯羧酸、乙烯磺酸和N-(3-羟苯基)甲基丙烯酰胺。另外，可用染料对共聚物官能化得到本发明的聚合物。

可溶于有机溶剂的抗反射聚合物可通过任何数量的结构 1 所描述的含有至少一个染料官能团的乙烯基单体，任何数量的不含交联官能团的如结构 2 描述的乙烯基单体反应而合成。可以聚合不同的带有不同取代基的结构 1 的染料单元和不同的结构 2 的单元形成一种具有所需刻蚀性能和和物理性能的聚合物。可以选择各单体上的取代基使由此形成的聚合物可溶于有机溶剂。其它不显著影响抗反射涂层的功能的不饱和单体也可加入到聚合混合物中。另外，可用染料对共聚物官能化得到本发明的聚合物。

用于聚合的方法可以是任何本领域公知的聚合乙烯基聚合物的方法，例如离子聚合或自由基聚合。形成的聚合物结构可以由交替、嵌段或无规聚合物组成。该聚合物的重均分子量范围为约 500 到约 1000000，优选约 1000 到约 100000，更优选约 3000 到约 40000。

单体可在有机溶剂中聚合，其中溶剂与抗反射涂料的流延溶剂相同，优选 PGMEA、PGME 或乳酸乙酯。

在最终聚合物中，含染料单体的摩尔％的范围为约 5％到 100％，且不含交联基团的一种或多种单体的摩尔％的范围为 0％到约 90％。此外，聚合物可能含有在聚合物制备的合成步骤中的未反应前体和/或单体。

涂料组合物包含本发明的聚合物和一种适用的溶剂或溶剂混合物。可加入其它组分增强涂层的性能，例如单体交联剂、单体染料、低级醇、交联促进添加剂、生酸剂(acid generator)、热活化生酸剂、酸、表面剂(surface leveling agent)、粘合促进剂、消泡剂等。交联剂的例子包括，但不限于，三聚氰胺、羟烷基酰胺、环氧树脂或胺固化环氧树脂、苯胍胺树脂、嵌段异氰酸酯、甘脲、二羟甲基苯、脲醛树脂和二乙烯基单体。在优选的实施方案中，涂料组合物包含本发明的聚合物、一种交联剂和溶剂。可使用的热活化生酸剂和酸是，但不限于，多羟基酚化合物的 2,1,4 重氮萘醌酯、烷基和芳基磺酸和酯、芳族磺酰胺、烷基和芳基磷酸和酯、或优选在高于 100℃的温度下热活化的热生酸剂。在抗反射涂料中也可加入单体染料，例如 Sudan 橙、

2,4-二硝基萘酚、姜黄素、香豆素等.

抗反射涂层对特定波长或波长范围的吸收可通过适当选择在染料官能团上的取代基而最优化. 吸电子或供电子基团的使用通常分别使吸收波长移向长波或短波方向. 此外, 抗反射聚合物在特别优选的溶剂中的溶解度可通过适当选择在单体上的取代基进行调节.

抗反射涂料组合物中聚合物的范围为溶液总重的约 1% 到约 40%. 精确的重量依聚合物的分子量和所需涂层的厚度而定. 典型的以混合物或单独形式使用的溶剂有丙二醇一甲醚(PGME)、丙二醇单甲醚乙酸酯(PGMEA)、乳酸乙酯、水、环戊酮、环己酮、和 γ-丁内酯, 但 PGME、PGMEA 和乳酸乙酯或其混合物是优选的. 具有低毒性、优异涂布和溶解性能的溶解通常是优选的.

由于抗反射膜涂布于基材的上面并进一步进行干蚀刻, 因此可以想见该膜应具有足够低的金属离子含量并具有一定纯度而对半导体设备的特性没有不良影响. 可以使用例如将聚合物溶液通过离子交换柱或阴离子或阳离子交换柱的组合、过滤、和萃取降低金属离子浓度并减小颗粒. 优选聚合物中每种金属离子的金属离子水平低于 50ppb, 更优选低于 10ppb 且再优选低于 1ppb.

抗反射涂料组合物通过本领域公知的技术涂布于基材上, 例如浸涂、旋涂或喷涂. 抗反射涂层的膜厚范围通常为约 0.1 微米到约 1 微米. 如果需要, 特别是对有起伏的基材进行平整, 也可以使用更厚的涂层, 特别是厚达 10 微米的涂层. 该涂层而后在电热板或对流传热炉中加热除去任何残余溶剂并使膜不溶解.

涂覆于抗反射膜上的光致抗蚀剂可以是任何半导体工业中使用的类型.

有两种类型的光致抗蚀剂组合物, 即负性(negative-work)和正性(positive-work). 当对负性光致抗蚀剂组合物进行图样的辐射曝光时, 暴露于辐射的抗蚀剂组合物的区域变得在显影剂溶液中较少地溶解(例如发生交联反应), 而未曝光的光致抗蚀剂组合物保持在该溶液中相对可溶. 因此, 用显影剂处理曝光后的负性抗蚀剂导致未曝光

区域的光致抗蚀剂涂层的去除，并在涂层上形成负相。如此剥离出下面的沉积有光致抗蚀剂组合物的基材的所需部分。

另一方面，当对正性光致抗蚀剂组合物进行图样的辐射曝光时，暴露于辐射的抗蚀剂组合物的区域变得在显影剂溶液较多地溶解（例如发生重排反应），而未曝光的光致抗蚀剂组合物保持在该溶液中相对不可溶。因此，用显影剂处理曝光后的正性抗蚀剂导致曝光区域的光致抗蚀剂涂层的去除，并在涂层上形成正相。同样，剥离出下面的基材所需部分。

目前正性光致抗蚀剂组合物相对负性抗蚀剂更为有利，因为前者通常具有更好的分辨力和图案转印性能。光致抗蚀剂的分辨率被定义为在曝光和显影之后，能够被抗蚀剂组合物从光掩膜转印到基材上的具有高度图像边缘锐度的最小特征。在许多现在的制造应用中，需要小于 1 微米的抗蚀剂分辨率。此外，几乎总是需要显影后的光致抗蚀剂的壁面轮廓相对基材接近垂直。抗蚀剂显影与未显影区域的这种划分表现为将掩膜图案精确地转印到基材上。这点在减小设备尺寸的微型化的驱使下变得更为关键。

正性光致抗蚀剂包含酚醛清漆树脂和用作光活性化合物的醌-二叠氮(quinone-diazide)化合物是本领域公知的。酚醛清漆树脂通常由甲醛与一种或多种多取代的酚在酸性催化剂，例如草酸的存在下缩合而制备。光活性化合物通常由多羟基酚化合物与萘醌二叠氮酸(naphthoquinone diazide acid)或其衍生物反应制备。这些种类的抗蚀剂的敏感范围通常为约 300nm 到 440nm。

可使用对约 180nm 到约 300nm 的短波长敏感的光致抗蚀剂。这些抗蚀剂通常包含聚羟基苯乙烯或取代的聚羟基苯乙烯衍生物、光活性化合物、和任选的溶解抑制剂。下面的参考中例举了所用的光致抗蚀剂的种类，在此将其引入本文作为参考：US4,491,628，US5,069,997 和 US5,350,660。

本发明的方法进一步包括用酚醛清漆树脂涂布基材，并在电热板或对流传热炉中在足够的温度下加热足够长时间去除涂层中的溶剂，

以使聚合物不溶解化到使其不溶于光致抗蚀剂的涂料溶剂或碱性显影剂水溶液中的程度。可使用多种本领域公知的基材，例如平坦的、有起伏的或有孔的基材。优选的温度范围为约 70℃到约 250℃，优选为约 100℃到约 200℃。如果温度低于 70℃时将出现不足的溶剂去除或不足的不溶解化作用；当温度温度高于约 250℃时聚合物变得化学不稳定。精确的温度应根据特定的应用而定。而后将光敏材料的膜涂覆于抗反射涂层之上，而后烘焙以基本除去光致抗蚀剂溶剂。光致抗蚀剂图样曝光并在显影剂水溶液中显影去除处理后的抗蚀剂。光致抗蚀剂的涂布和成像对本领域熟练技术人员是公知的，并根据所使用的抗蚀剂的具体种类进行优化。形成图案的基材而后进行干蚀刻。蚀刻可以在合适的蚀刻室中进行，除去抗反射膜的曝光部分，其中保留的光致抗蚀剂用作蚀刻掩膜。可包括任选的加热步骤优化蚀刻方法。可使用本领域公知的多种蚀刻技术。

在抗反射涂层和光致抗蚀剂之间可放置中间层防止层间混合，并显而易见属于本发明的范围之内。中间层是溶剂流延的惰性聚合物，其中聚合物的例子是聚砜和聚酰亚胺。

另一种需要底涂层（例如本发明的底涂层）的方法是对光致抗蚀剂层甲硅烷基化制备一种用于蚀刻底涂层的蚀刻抗蚀剂掩膜的方法。该方法包括在基材上形成带有使用本发明的组合物的底涂层的涂层、形成光敏层、使该光敏层成像和显影、用合适的甲硅烷基化试剂对光敏层甲硅烷基化、及用甲硅烷基化的光敏层图像作为掩膜蚀刻底涂层。甲硅烷基化的概念对本领域的熟练技术人员是公知的，并描述于参考文献 Sebald 等人 SPIE, Vol. 1262, 第 528-537 页, 1990 中。如本领域所公知的，将要进行甲硅烷基化的光致抗蚀剂应设计为有甲硅烷基化能力的那些。由于其优异的蚀刻性能，已经发现本发明的底涂层特别适用于此方法。

随后的具体实施例将对本发明的组合物制备和应用的方法作出详细的说明。然而，这些实施例并不是用来对本发明的保护范围作任何的限定或限制，并不能认为是为实施本发明所必须使用的条件、参数

或变量。

实施例

实施例 1. 聚合物 1 的制备

向 1 升的圆底烧瓶中顺序加入 360ml 甲醇、60ml 浓盐酸、和 50g 氨基苯甲酸乙酯。将该溶液冷却至 10℃并在搅拌下向烧瓶中加入 35g 亚硝酸异丁酯。立即发生重氮化反应。亚硝酸异丁酯加入完毕后，溶液在 10℃中储存并准备进行偶联反应。

向 2 升烧瓶中加入 65.5g 乙酰乙酸 2-(甲基丙烯酰氧)乙基酯(MEAA)、65g 吡啶、和 1.2 升甲醇。将该溶液冷却至 10℃并将上述重氮盐加入反应器中。立即生成偶联产物并沉淀形成悬浮液。重氮盐加入完毕后，将反应器升温至室温。过滤得到黄色固体 4-乙氧基羰基苯基偶氮偶联产物(ECP)，产率 90%。

在 1 升烧瓶中，将 100gECP 溶解在四氢呋喃(THF)中。该溶液通过向其中通入氮气鼓泡约 1 小时进行脱气。向该溶液中注入 17g 甲基丙烯酸甲酯（MMA）和 2,2'-偶氮二异丁腈（AIBN）（1.4g）的 THF 溶液，该聚合化合物进一步脱气 30 分钟。移去排气针(outlet needle)，密封容器在 65℃下搅拌 20 小时。而后溶液在 5 升 2-丙醇中沉降。得到黄色固体的聚合物，产率 95%。聚合物在乳酸乙酯中的 UV-可见光光谱表明在 356nm 处有最大吸收（λ_{max}）。凝胶渗透色谱表明聚合物具有 32769 的重均分子量（Mw）。

实施例 2. 聚合物 2 的制备

向 1 升的圆底烧瓶中顺序加入 360ml 甲醇、60ml 浓盐酸、和 45.5g 4-氨基乙酰苯胺。将该溶液冷却至 10℃并在搅拌下向烧瓶中加入 35g 亚硝酸异丁酯。立即发生重氮化反应。亚硝酸异丁酯加入完毕后，溶液在 10℃中储存并准备进行偶联反应。

向 2 升烧瓶中加入 65.5g 乙酰乙酸 2-(甲基丙烯酰氧)乙基酯、65g 吡啶、和 1.2 升甲醇。将该溶液冷却至 10℃并将上述重氮盐加入反应器中。立即生成偶联产物并沉淀形成悬浮液。重氮盐加入完毕后，将反应器升温至室温。过滤得到黄色固体 4-乙酰基氨基苯基偶氮偶联产

物(AAP)，产率 90%。

在 1 升烧瓶中，将 100gAAP 溶解在四氢呋喃(THF)中。该溶液通过向其中通入氮气鼓泡约 1 小时进行脱气。而后向该溶液中注入 AIBN（1.4g)的 THF 溶液，该聚合化合物进一步脱气 30 分钟。移去排气针，密封容器在 65℃下搅拌 20 小时。而后溶液在 5 升 2-丙醇中沉降。得到黄色固体的聚合物，产率 94%。聚合物在乳酸乙酯中的 UV-可见光光谱表明 λ_{max} 位于 389nm 处。凝胶渗透色谱表明聚合物具有 13100 的重均分子量（Mw）。

实施例 3-8. 聚合物 3-8 的制备

表 1 中表明根据实施例 1 描述的步骤制备聚合物，以及这些聚合物在乳酸乙酯（EL）中的吸收峰（λ_{max}）和消光系数（ε）。

表 1

聚合物#	AAP 摩尔%	ECP 摩尔%	MEAA 摩尔%	MMA (摩尔%)	GPC (Mw)	λmax (nm)	ε (L/g.cm)
2	100				13,100	389	59
3		100			40,357	356	60
4	70			30	6,479	389	49
5		75	25		44,196	356	52
6		60		40	32,000	356	53
7		34	66		19,024	356	28
8		30	40	30	42,092	356	31

实施例 9. 聚合物 9 的制备

向 1 升的圆底烧瓶中顺序加入 200ml 甲醇、40ml 浓盐酸、和 25g 氨基苯甲酸乙酯。将该溶液冷却至 10℃并在搅拌下向烧瓶中加入 18g 亚硝酸异丁酯。立即发生重氮化反应。亚硝酸异丁酯加入完毕后，溶液在 10℃中储存并准备进行偶联反应。

向 1 升烧瓶中加入 32.0g 乙酰乙酸 2-(甲基丙烯酰氧)乙基酯、35g 吡啶、和 700 毫升甲醇。将该溶液冷却至 10℃并将上述重氮盐加入反应器中。立即生成偶联产物并沉淀形成悬浮液。重氮盐加入完毕后，将反应器升温至室温。过滤得到 ECP 固体，产率 92%。

在 1 升烧瓶中，将 50g 上述黄色固体溶解在 THF 中。该溶液通过向其中通入氮气鼓泡约 1 小时进行脱气。然后向该溶液中注入 27g 甲基丙烯酸甲酯、29.6g 马来酸酐和 AIBN（2.35g）的 THF 溶液，该聚合化合物进一步脱气 30 分钟。移去排气针，密封容器在 65℃下搅拌 20 小时。而后溶液在 5 升 2-丙醇中沉降。得到黄色固体的聚合物，产率 96％。聚合物在乳酸乙酯中的 UV-可见光光谱表明 λ_{max} 位于 356nm。GPC 表明聚合物具有 8044 的 Mw。

实施例 10-14

向 4.0g 表 2 中所示的每种聚合物和 96.0g 丙二醇单甲醚乙酸酯(PGMEA)的溶液中加入 0.48gCYMEL®303 和 0.04gCYCAT®600（两种均购自 CYTEC Industries, Inc.）。该溶液以 3000rpm 旋涂于 4 英寸的硅晶片上，并在 180℃的电热板上烘焙 60 秒。涂覆的晶片随后浸渍于多种抗蚀剂流延溶剂中，例如 PGMEA 和 EL 中 60 秒，而后旋转干燥。浸渍前后的膜厚用 NANOSPECAFT 测量。聚合物和溶剂之间的层间混合的程度用聚合物膜厚的变化测量，列于表 2。显然本发明的聚合物在典型光致抗蚀剂流延溶剂中的溶解度是可以忽略的。

表 2

实施例	聚合物	溶剂	T_1(A)	T_2(A)
10	1	PGMEA	748	747
11	1	EL	740	743
12	3	PGMEA	801	798
13	4	PGMEA	723	723
14	5	PGMEA	776	769

其中，

T1：溶剂浸渍之前的聚合物膜厚

T2：溶剂浸渍之后的聚合物膜厚

实施例 15

将实施例 10 和 12-14 中形成的聚合物溶液旋涂于 4 英寸的硅晶片上，并在 180℃的电热板上烘焙 60 秒，得到约 850Å 的厚度。而后用

AZ®7908 光致抗蚀剂(购自 Clariant Corporation, 70 Meister Ave., Somerville, NJ08876)涂覆，并在 90℃下烘焙 90 秒得到 0.974μm 的厚度。一个涂覆有 0.974μm 厚 AZ®7908 光致抗蚀剂并在 90℃下烘焙 90 秒的 4 英寸晶片用作参比.

这些晶片用 NIKON® 0.54NA i-line stepper 在一定辐射范围内图样曝光. 曝光后的晶片在 110℃烘焙 60 秒，并用 AZ®300MIF Developer (购自 Clariant Corporation, 70 Meister Ave., Somerville, NJ 08876)搅炼(puddle)显影 35 秒. 在这些晶片上形成的抗蚀图像用 Hitachi S-4000 场致发射扫描电子显微镜评测。表 3 说明使用或不使用本发明的抗反射底涂层的 AZ®7908 光致抗蚀剂的刻蚀性能的比较. 本发明的聚合物底涂层在不牺牲光敏性能下，显著地提高了分辨率并有效的消除了由于晶片基材的反射造成的驻波(standing wave)。

表 3

底涂层	DTP(mj/cm2)	分辨率(μm)	驻波
实施例 10	175	0. 28	消除
实施例 12	180	1. 0.28	消除
实施例 13	175	2. 0.30	消除
实施例 14	175	3. 0.30	消除
无	170	4. 0.38	严重

其中 DTP 为影印剂量.

实施例 16

将实施例 10, 13 和 14 中形成的聚合物溶液旋涂于 4 英寸的硅晶片上，并在 180℃的电热板上烘焙 60 秒，得到约 850Å 的厚度。而后用 AZ®7908 光致抗蚀剂(购自 Clariant Corporation, 70 Meister Ave., Somerville, NJ08876)涂覆，并在 90℃下烘焙 90 秒得到 0.75μm 到 1.10μm 的抗蚀剂厚度。这些晶片用 NIKON® 0.54NA i-line stepper 图样曝光。曝光后的晶片在 110℃烘焙 60 秒，并用 AZ®300MIF Developer 搅炼显影 35 秒。清除膜所需的最小剂量作为抗蚀剂厚度的函数作图，由此得到的正弦曲线称为摆动曲线(swing curve)。光致抗

蚀剂的摆动比与在半导体工业中经常遇到的高反射基材或有起伏的基材上的光致抗蚀图像的线宽变化密切相关。摆动比越小，对反射基材或起伏基材的线宽控制越好。摆动比例用下式计算:

$$\text{摆动比} = (E_{max} - E_{min}) / (E_{max} + E_{min})$$

其中，

Emax 和 Emin 对映于摆动曲线中最大值和最小值处的抗蚀剂厚度的清除剂量。摆动曲线通过清除显影后的抗蚀剂膜所需的剂量作为抗蚀剂厚度的函数作图得到。

$$\%\text{摆动减小} = \frac{(\text{硅上的摆动比} - \text{聚合物上的摆动比})}{\text{硅上的摆动比}}$$

其中，硅上的摆动比与聚合物上的摆动比分别对映于涂覆于硅晶片和聚合物底涂层上的光致抗蚀剂的摆动比。

涂覆于本发明聚合物涂层上的 AZ®7908 光致抗蚀剂的%摆动减小列于表 4 中。

表 4

底涂层	%摆动减小
无	0
实施例 10	88
实施例 13	75
实施例 14	85

显然，本发明的聚合物涂层可以有效地降低光致抗蚀剂的摆动比。

实施例 17

用 30 重量%的 Mw 为约 17000 的聚合物 8 的乳酸乙酯溶液涂布硅晶片。该硅晶片在 170℃下加热 60 秒得到 4 微米的涂层。而后该晶片用 AZ®CP365 光致抗蚀剂（购自 Clariant Corporation）涂布，并在 110℃下烘焙 60 秒.该基材用 I-line stepper 在 80mJcm^{-2}到 150mJcm^{-2}的不同曝光能量下成像。潜影用 AZ®300 MIF 显影剂以流动/搅炼模式(stream/puddle)显影 60 秒。用 2 重量%的 Tegomer 溶液硅氧烷聚合物（购自 Shin-Etsu Coropration）己醇处理 2 分钟完成甲烷基化作

用。用带有氧气和氢气的反应性离子蚀刻将图案转印到基材上。二次(secondary)电子显微图像表明完全的图像转印。