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(57) Abstract

The present invention relates to a novel antireflecting coating composition, where the composition comprises a polymer, thermal acid generator and a solvent composition. The invention further comprises processes for the use of such a composition in photolithography. The composition strongly absorbs radiation ranging from about 130 nm (nanometer) to about 250 nm.

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Description

Antireflective Composition for a Deep Ultraviolet Photoresist

Background

The present invention relates to novel antireflective coating compositions and their use in image processing by forming a thin layer of the novel antireflective coating composition between a reflective substrate and a photoresist coating. Such compositions are particularly useful in the fabrication of semiconductor devices by photolithographic techniques, especially those requiring exposure with deep ultraviolet radiation.

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 miniaturization of semiconductor devices has lead to the use of new photoresists that are sensitive to lower and lower wavelengths of radiation and has also lead to the use of sophisticated multilevel systems to overcome difficulties associated with such miniaturization.

High resolution, chemically amplified, deep ultraviolet (100-300 nm) positive and negative tone photoresists are available for patterning images with less than quarter micron geometries. There are two major deep ultraviolet (uv) exposure technologies that have provided significant advancement in miniaturization, and these are lasers that emit radiation at 248nm and 193nm. Examples of such photoresists are given in the following patents and incorporated herein by reference, US 4,491,628, US 5,350,660, EP 794458 and GB 2320718. Photoresists for 248 nm have typically been based on substituted polyhydroxystyrene and its copolymers. On the other hand, photoresists for 193 nm exposure require non-aromatic polymers, since aromatics are opaque at this wavelength. Generally, alicyclic hydrocarbons are incorporated into the polymer to replace the etch resistance lost by not having aromatics present. Furthermore, at lower wavelengths the reflection from the substrate becomes increasingly detrimental to the lithographic performance of the photoresist. Therefore, at these wavelengths antireflective coatings become critical.

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 major disadvantages of back reflectivity are thin film interference effects and reflective notching. Thin film interference, or standing waves, result in changes in critical line width dimensions caused by variations in the total light intensity in the resist film as the thickness of the resist changes. Reflective notching becomes severe as the photoresist is patterned over substrates containing topographical features, which scatter light through the photoresist film, leading to line width variations, and in the extreme case, forming regions with complete photoresist 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 substantially eliminate it.

In addition, dyed resists also 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 line width variation is required, the use of bottom antireflective coating provides the best solution for the elimination of reflectivity. The bottom 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 plasma, and the resist pattern is thus transferred to the substrate. The etch rate of the antireflective film should be relatively high in comparison to the photoresist so that the antireflective film is etched without excessive loss of the resist film during the etch process. Inorganic types of antireflective coatings include such films as TiN, TiON, TiW and spin-on organic polymer in the range of 30 NM, and are discussed in the following papers: C. Nolscher et al., Proc SPIE vol. 1086, p242 (1989); K. Bather, H. Schreiber, Thin solid films, 200, 93, (1991); G. Czech et al., Microelectronic Engineering, 21, p.51 (1993). Inorganic B.A.R.C.s require precise control of the film thickness, uniformity of film, special deposition equipment, complex adhesion promotion techniques prior to resist coating, separate dry etching pattern transfer step, and dry etching for removal.

Organic B.A.R.C.s are more preferred and have been formulated by adding dyes to a polymer coating (Proc. SPIE, Vol. 1086 (1989), p. 106). Problems of such dye blended coatings include 1) separation of the polymer and dye components during spin coating 2) dye stripping into resist solvents, and 3) thermal diffusion into the resist upon the baking process. All these effects cause degradation of photoresist properties and therefore are not the preferred composition.

Light absorbing, film forming polymers are another option. Polymeric organic antireflective coatings are known in the art as described in EP 583,205, and incorporated herein by reference. However, the antireflective films as disclosed in EP 583,205 are cast from organic solvents, such as cyclohexanone and cyclopentanone. The potential hazards of working with such organic solvents, have lead to the development of the antireflective coating composition such as those disclosed in US 5,652,317, 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 ether acetate (PGMEA), propylene gycol monomethyl ether (PGME), and ethyl lactate (EL). Another advantage of using antireflective coatings soluble in the preferred, lower toxicity solvents, is that these same solvents can also be used to remove the edge bead of the antireflective coating and no additional hazards or equipment expense is incurred, since these solvents are also used for photoresist and photoresist processing. The polymers of the inventions disclosed in the prior art, constitute polymers where the chromaphore is pendant from the backbone of the polymer and where the chromophore, which is typically aromatic, absorbs at wavelengths such as 436 nm, 365 nm and 248 nm, where the photoresist is exposed. These polymers have been found to be ineffective when used as antireflective coatings for photoresists sensitive to 193 nm. It is believed that such antireflective polymers are very aromatic in nature and thus are too reflective, acting as a mirror rather than absorbers. Additionally, these polymers being highly aromatic, have too low a dry etch rate, relative to the new type of non-aromatic photoresists used for 193 nm exposure, and are therefore ineffective for imaging and etching. Photoresist patterns may be damaged or may not be transferred exactly to the substrate if the dry etch rate of the antireflective coating is similar to or less than the etch rate of the photoresist coated on top of the antireflective coating.

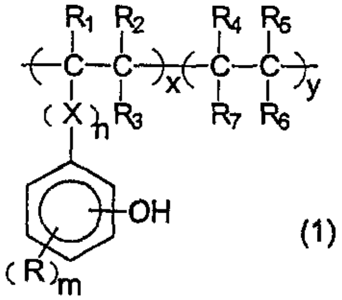
The antireflective composition disclosed in EP 542 008, is based on highly aromatic polymers, such as novolaks, polyvinyl phenols, copolymers of polyvinyl phenol and styrene or alphamethyl styrene, etc. Furthermore, this antireflective coating must be able to crosslink with the photoresist, where the photoresist is based on a polyvinylphenol resin sensitive at 248 nm. However, the high degree of aromaticity in the antireflective coating and the photoresist and the low etch rates of novolaks, polyvinylphenols, etc. are detrimental to the imaging process at 193 nm. Therefore, it is necessary to have a bottom antireflective coating that functions well at exposures less than 230 NM.

The novel antireflective coatings of the present invention have been found to have good dry etching properties, which enable a good image transfer from the photoresist to the substrate, and also good absorption characteristics to prevent reflective notching and line width variations or standing waves, particularly at 193 nm. Additionally, substantially no intermixing is present between the antireflective coating and the photoresist film. The antireflective coatings also have good solution stability and form particularly thin films with good coating quality, the latter being particularly advantageous for lithography. When the antireflective coating is used with a photoresist in the imaging process, clean images are obtained.

Summary

The present invention relates to a novel antireflecting coating composition suitable for use with a photoresist, where the composition comprises a copolymer, thermal acid generator and a solvent composition. The invention further comprises processes for the use of such a composition in photolithography. The composition strongly absorbs radiation ranging from about 130 nm (nanometer) to about 250 nm.

The polymer of the novel composition has the structure,


(1)

where,

X is CO_2, O or SO_2 and n=0 or 1, x is an integer and y is 0 or an integer, providing when n=0, y is an integer,

R is hydrogen, halogen, nitro, alkyl(C_1-C_4), alkoxy(C_1-C_4) or esters(C_1-C_4), and, m=1-4,

R_1 to R_7 are independently hydrogen, halogen, alkyl(C_1-C_4), alicyclic group, alkoxy(C_1-C_4), esters(C_1-C_4), CO_2 (alkyl)OH, CO_2(alkyl)$COCH_2COCH_3$, further where R_7 and R_6 are combined to form a saturated ring or anhydride.

Preferably the polymers are poly(hydroxystyrene-methyl methacrylate), poly(hydroxyphenyl methacrylate- methyl methacrylate), poly(hydroxyphenyl methacrylate) or mixtures thereof.

The thermal acid generator is activated above 90°C, preferably above 150°C and more preferably above 190°C.

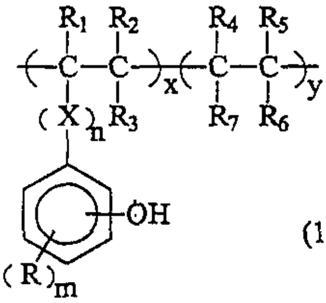
The solvents of the novel composition are organic solvents, in particular solvents that are of low toxicity and additionally have good coating and solubility properties. The preferred choice of organic solvents that are well known for having low toxicity and are also useful for dissolving the solid components of the present composition, are propylene gycol monomethyl ether acetate (PGMEA), propylene gycol monomethyl ether (PGME), ethyl lactate (EL), and 2-heptanone, although other low toxicity solvents can also be used alone or as mixtures.

The invention also relates to an article comprising a substrate with a layer of the novel antireflective coating composition and having thereon a coating of photoresist comprising a non-aromatic polymer, a photoactive compound and a photoresist solvent.

The invention further comprises a process for 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 130 nm to about 300 nm, preferably comprising a non-aromatic polymer sensitive at 193 nm, and processed in an aqueous alkaline developer to give a photoresist pattern. Preferably the photoresist comprises a non-aromatic polymer, a photoactive compound and a photoresist solvent. 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-containing plasma, with the photoresist pattern acting as an etch mask.

Detailed Description

The present invention relates to a novel antireflecting coating composition, where the composition comprises a polymer, a crosslinker, a thermal acid generator and a solvent composition. The invention further comprises processes for the use of such a composition in photolithography. The polymer of the novel composition has the structure,



(1)

where,

X is CO_2, O or SO_2 and n=0 or 1, x is an integer and y is 0 or an integer, providing when n=0, y is an integer,

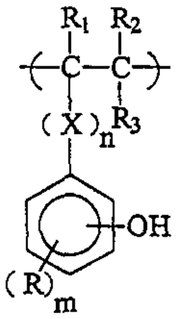
R is hydrogen, halogen, nitro, alkyl(C_1-C_4), alkoxy(C_1-C_4) or esters(C_1-C_4), and, m=1-4,

R_1 to R_7 are independently hydrogen, halogen, alkyl(C_1-C_4), alicyclic group, alkoxy(C_1-C_4), esters(C_1-C_4), CO_2 (alkyl)OH, CO_2(alkyl)$COCH_2COCH_3$, further where R_7 and R_6 are combined to form a saturated ring or anhydride.

The polymer is particularly effective in absorbing radiation in the deep ultraviolet region, more particularly at about 193nm.

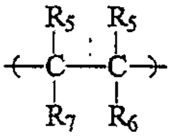
The polymer of this invention can be a homopolymer of only the phenolic unit, where X is represented by CO_2, O or SO_2, n = 1 and y = 0. An example of such a homopolymer is poly(hydroxyphenyl methacrylate). The invention excludes polyhydroxystyrene or novolaks as the main polymeric component.

The polymer of this invention can also include copolymers comprising at least one recurring phenolic unit with the structure (2)



(2)

and at least one recurring nonaromatic unit with the structure



$$-\!\left(\overset{R_5}{\underset{R_7}{C}}-\overset{R_5}{\underset{R_6}{C}}\right)\!-$$

(3)

The phenolic unit provides both a crosslinking site as well as a chromophore for absorption in the deep uv region. The hydroxyl group is preferably in the ortho or para position, more preferably in the para position. Other substituents may also be present on the aromatic ring, as long as they are not aromatic and do not contain any conjugation that would lead to absorption in the long ultraviolet, i.e. 320 nm to 450 nm. Excluded would be substituent groups such as -N=N- or -C=C-, which are conjugated to a phenol. It is preferred that substituents to the aromatic ring are hydrogen, alkyl, alkoxy, esters, nitro or halogen; examples of which are methyl, ethyl, propyl, isopropyl, butyl, t-butyl, methoxy, ethoxy, propoxy, butoxy, acetoxy and chloro, more preferably hydrogen, nitro or alkyl. The phenol may be attached directly to the backbone or through the connecting group, X, where X is CO_2, SO_2 or O, preferably CO_2. The copolymer may comprise a single type of phenolic unit or a mixture of two or more types of phenolic units depending on the characteristics desired for the antireflective coating. Different substituents may be used to enhance certain properties, such as, for example, adhesion, solubility, absorbance and film-forming properties. Preferred phenolic monomers for polymerization with the nonaromatic monomer are hydroxystyrene, hydroxyphenyl methacrylate, or mixtures thereof.

The nonaromatic unit may be any unsaturated unit that does not contain aromatic groups. Specific examples of the comonomer useful for polymerization are acrylic or methacrylic acid, acrylates, methacrylates, maleic anhydride, acrylonitrile, vinyl ethers, etc. The nonaromatic comonomer may be used alone or as a mixture of two or more nonaromatic comonomers depending on the characteristics desired for the antireflective coating. Different substituents may be used to enhance certain properties, such as, for example, adhesion, solubility, absorbance and film-forming properties.

The ratio of the phenolic unit and the nonaromatic unit in the copolymer may be varied according to the properties required for the antireflective coating, preferably the phenolic unit ranges from about 35 mole % to about 65 mole %, and more preferably from about 45 mole % to about 55 mole %, particularly where hydroxystyrene or its derivatives are used as the phenolic monomer.

The absorption parameter (k) of the novel composition at 193 nm ranges from about 0.3 to about 0.7, preferably from about 0.5 to about 0.65 as measured using ellipsometry. The value of the refractive index (n) ranges from about 1.25 to about 1.9. Due to the good absorption characteristics of this composition at 193 nm, very thin antireflective films of the order of about 40 nm may be used. This is particularly advantageous when using a nonaromatic photoresist, such as those sensitive at 193 nm, where the photoresist films are thin and must act as an etch mask for the antireflective film. Preferably the film thickness of the antireflective coating is less than 150 nm, and more preferably it is less than 90 nm.

The polymers of this invention may be prepared by any of the standard polymerization methods known in the art, examples of such methods are free radical, anionic or cationic copolymerization techniques. The polymer may be synthesized using solution, emulsion, bulk, suspension polymerization, or the like. The polymer may also be synthesized from capped monomers, for example where the hydroxyl group of the phenolic monomer is blocked with a group like acetoxy before polymerization, and then the capping group is hydrolyzed after the polymer has been synthesized thereby giving the polymer of the present novel composition. The copolymer may have various structures, such as random, block, graft, etc. The weight average molecular weight of the polymer may range from 1500 to about 50,000, preferably 4,000 to about 30,000 and more preferably 5,000 to about 20,000. When the weight average molecular weight is below 1,500, then good film forming properties are not obtained for the antireflective coating and when the weight average molecular weight is too high, then properties such as solubility, storage stability and the like may be compromised.

A variety of crosslinking agents can be used in the composition of the present invention. Any suitable crosslinking agent that can crosslink the polymer in the presence of an acid may be used. Examples of such crosslinking agents are melamines, methylols, glycoluril, hydroxy alkyl amides, epoxy and epoxy amine resins, blocked isocyanates, and divinyl monomers. Melamines like hexamethoxymethyl melamine; glycolurils like tetrakis(methoxymethyl)glycoluril; and aromatic methylols, like 2,6 bishydroxymethyl p-cresol are preferred.

The thermal acid generator of the present invention, is a compound which, when heated to temperatures greater than 90°C and less than 250°C, generates an acid. The acid, together with the crosslinker, crosslinks the polymer. The antireflective film after heat treatment becomes insoluble in the solvents used for coating photoresists, and furthermore, is also insoluble in the alkaline developer used to image the photoresist. Preferably, the thermal acid generator is activated at 90°C and more preferably at 150°C, and even more preferably at 190°C. The antireflective film is heated for a sufficient length of time to crosslink the coating. Examples of thermal acid generators are nitrobenzyl tosylates, such as 2-nitrobenzyl tosylate, 2,4-dinitrobenzyl tosylate, 2,6-dinitrobenzyl tosylate, 4-nitrobenzyl tosylate; nitrobenzyl benzenesulfonates such as 2-trifluoromethyl-6-nitrobenzyl 4-chlorobenzenesulfonate, as 2-trifluoromethyl-6-nitrobenzyl 4-nitro benzenesulfonate; phenolic sulfonate esters such as phenyl, 4-methoxybenzenesulfonate.

Thermal acid generators are preferred over free acids, although free acids may also be used, in the novel antireflective composition, since it is possible that over time the shelf stability of the antireflective solution will be effected by the presence of the acid, if the polymer were to crosslink in solution. Thermal acid generators are only activated when the antireflective film is heated on the substrate. Although thermal acid generators are preferred for crosslinking the polymer efficiently, an antireflective composition comprising the polymer and crosslinking agent may also be used, where heating crosslinks the polymer.

The amount of the copolymer in the present composition can vary from about 90 weight % to about 50 weight %, preferably about 85 weight % to about 70 weight % and more preferably about 80 weight % to about 70 weight %, relative to the solid portion of the composition. The amount of the crosslinker in the present composition can vary from 5 weight % to about 50 weight %, preferably 15 weight % to about 30 weight % relative to the solid portion of the composition. The amount of the thermal acid generator in the present composition can vary from 0.1 weight % to about 5 weight %, preferably 0.5 weight % to about 3 weight % and more preferably 1 weight % to about 2 weight %, relative to the solid portion of the composition.

Typical solvents, used as mixtures or alone, that can be used for the present composition are propylene gycol monomethyl ether acetate (PGMEA), propylene gycol monomethyl ether (PGME), and ethyl lactate (EL), 2-heptanone, cyclopentanone, cyclohexanone, and gamma butyrolactone, but PGME, PGMEA and EL or mixtures thereof are preferred. Solvents with a lower degree of toxicity, good coating and solubility properties are generally preferred.

The antireflective coating composition comprises the copolymer, crosslinker and thermal acid generator 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 dyes, lower alcohols, surface leveling agents, adhesion promoters, antifoaming agents, etc. Other polymers, such as, novolaks, polyhydroxystyrene, polymethylmethacrylate and polyarylates, may be added to the composition, providing the performance is not negatively impacted. Preferably the amount of this polymer is kept below 50 weight % of the total solids of the composition, more preferably 20 weight %, and even more preferably below 10 weight %.

Since the antireflective film is coated on top of the substrate and is further subjected to dry etching, it is envisioned that the film is of sufficiently low metal ion level and of sufficient 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, filtration, and extraction processes can be used to reduce the concentration of metal ions and to reduce particles.

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 ranges from about 20 nm to about 200 nm. The optimum film thickness is determined, as is well known in the art, to be where no standing waves are observed in the photoresist. It has been unexpectedly found that for this novel composition very thin coatings can be used due to the excellent absorption and refractive index properties of the film. The coating is further heated on a hot plate or convection oven for a sufficient length of time to remove any residual solvent and induce crosslinking, and thus insolubilizing the antireflective coating to prevent intermixing between the antireflective coating and the photoresist layer.

Photoresists can be any of the types used in the semiconductor industry, provided the photoactive compound in the photoresist and the antireflective coating absorb at the exposure wavelength used for the imaging process.

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 push toward miniaturization reduces the critical dimensions on the devices.

Photoresists sensitive to short wavelengths, between about 130 nm and about 250 nm can also be used where subhalfmicron geometries are required. Particularly preferred are photoresists comprising non-aromatic polymers, a photoacid generator, optionally a solubility inhibitor, and solvent. Photoresists sensitive at 193 nm that are known in the prior art are described in the following references and incorporated herein, EP 794458, WO 97/33198 and US 5,585,219, although any photoresist sensitive at 193 nm may be used on top of the antireflective composition of this invention.

The process of the instant invention further comprises coating a substrate with the novel antireflective coating and heating on a hotplate or convection oven at a sufficiently high temperature for sufficient length of time to remove the coating solvent, and crosslink the polymer to a sufficient extent so that the coating is not soluble in the coating solution of the photoresist or in the aqueous alkaline developer. An edge bead remover may be applied to clean the edges of the substrate using processes well known in the art. The preferred range of temperature is from about 90°C to about 250°C. If the temperature is below 90°C then insufficient loss of solvent or insufficient amount of crosslinking takes place, and at temperatures above 250°C the composition may become chemically unstable. A film of photoresist 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 photoresist. The developer is preferably an aqueous alkaline solution comprising, for example, tetramethyl ammonium hydroxide. 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 can then be dry etched in a suitable etch chamber to remove the exposed portions of the antireflective film, with the remaining photoresist acting as an etch mask.

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 polysulfones and polyimides.

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.

Example 1

The photoresist used for coating on top of the antireflective coating of this invention was formulated with 3.311 g of a copolymer of mevalonic lactone methacrylate and 2-methyladamantyl methacrylate, 0.1361 g of diphenyliodonium nonafluoro-1-butanesulfonate, 0.00265 g of piperdine ethanol and 20 g of ethyl lactate. The solution was filtered with 0.45 and 0.2 µm filters. 500 nm thick photoresist solution was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed unacceptable standing waves.

Example 2 (comparative)

An antireflective coating composition was made by dissolving 1.0 g of poly(4-hydroxystyrene, 0.299 g of tetrakis(methoxymethyl)glycoluril (Powderlink® available from Cytec Industries, West Paterson, New Jersey), 0.013 g of p-nitrobenzyl tosylate were dissolved in 49.0 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 µm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained by baking a silicon wafer coated with the antireflective composition at a temperature of 220°C for 60 seconds then analyzed by spectroscopic ellipsometry on a J.A. Woollam®VASE spectroscopic ellipsometer in the 185 to 1000 nm range. Data were collected at 450 wavelengths under 6 angles of incidence (55-80° in steps of 5°), resulting in over 2500 separate ellipsometric measurements. All measurements used dynamic averaging. Dynamic averaging is useful in the DUV range where the lamp output is highly decreased.

Initially, the film was analyzed in the wavelength range >400 nm, assuming the film to be a pure dielectric (i.e., transparent). This analysis resulted in the determination of one unknown, film thickness, as well as a set of Cauchy coefficients describing the real part of the refractive index n for the long wavelength range. With the film thickness known from the earlier analysis, the data were then analyzed at each wavelength, leading to a set of dispersion curves n (refractive index) and k (absorption parameter) for each film. Each film was analyzed using this method. The refractive index was found to be 1.73 and the absorption parameter was 0.9013.

The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. Standing waves were observed in the photoresist images.

Example 3

An antireflective coating composition was made by dissolving 6 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 1.8 g of 2,6 bishydroxymethyl p-cresol and 0.078 g of p-toluene sulfonic acid monohydrate in 48 g of 1:1 mixture of ethyl lactate and propylene glycol monomethyl ether acetate. The solution was filtered through 0.45 and 0.2 µm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.466 and the absorption parameter was 0.576. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be less than 1.8%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 4

An antireflective coating composition was made by dissolving 3 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 0.9 g of 2,6 bishydroxymethyl p-cresol and 0.0039 g of p-toluene sulfonic acid monohydrate in 27 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 µm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.466 and the absorption parameter was 0.576. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 5

An antireflective coating composition was made by dissolving 3 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 0.9 g of 2,6 bishydroxymethyl p-cresol and 0.0039g of p-nitrobenzyl tosylate in 27 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 μm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.466 and the absorption parameter was 0.576. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt %

aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 6

An antireflective coating composition was made by dissolving 3 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 0.9 g of Cymel® 324 (available from Cytec Industries Inc. West Paterson, New Jersey) and 0.0195 g of p-nitrobenzyl tosylate in 27 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 μm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.466 and the absorption parameter was 0.576. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 7

An antireflective coating composition was made by dissolving 0.75 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 0.112 g of

Cymel® 324 (available from Cytec Industries, West Paterson, New Jersey) and 0.1 12 g of 2,6-bis(hydroxymethtyl p-cresol) and 0.0097 g of p-nitrobenzyl tosylate were dissolved in 36.25 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 µm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.452 and the absorption parameter was 0.555. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 8

An antireflective coating composition was made by dissolving 0.75 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 0.224 g of tetrakis(methoxymethyl)glycoluril (Powderlink®, available from Cytec Industries, West Paterson, New Jersey) and 0.0097 g of p-nitrobenzyl tosylate in 36.25 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 µm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.442 and the absorption parameter was 0.532. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 9

An antireflective coating composition was made by dissolving 0.75 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 0.13 g of hexamethoxymethyl melamine and 0.0097 g of p-nitrobenzyl tosylate in 36.25 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 μm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.445 and the absorption parameter was 0.545. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 10

An antireflective coating composition was made by dissolving 0.75 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 0.224 g of hexamethoxymethyl melamine and 0.0195 g of p-nitrobenzyl tosylate in 36.25 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 μm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.455 and the absorption parameter was 0.536. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 11

An antireflective coating composition was made by dissolving 0.75 g of poly(4-hydroxystyrene-co-methyl methacrylate (52:48)), 0.32 g of tetrakis(methoxymethyl)glycoluril (Powderlink®, available from Cytec Industries, West Paterson, New Jersey), 0.0214 g of p-nitrobenzyl tosylate were dissolved in 36.40 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 μm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.456 and the absorption parameter was 0.542. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 12

35.6 g (0.2 mol) of 2-hydroxyphenyl methacrylate, 5.01 (0.05 mol) g of methyl methacrylate were dissolved in 60.92 g of dry tetrahydrofuran and to this solution was added 4.06 g of 2,2'-azobisisobutyronitrile (AIBN). The contents were stirred at 70°C under nitrogen atmosphere for 5 hours. The viscous solution was poured in to isopropanol and the precipitate washed and re-precipitated two more times in isopropanol. Thus 40 g of polymer was isolated, dried under vacuum.

Example 13

An antireflective coating composition was made by dissolving 1.0 g of poly(2-hydroxyphenyl methacrylate-co-methyl methacrylate) prepared in Example 12 and 0.32 g of tetrakis(methoxymethyl)glycoluril (Powderlink® available from Cytec Industries, West Paterson, New Jersey), 0.013 g of p-nitrobenzyl tosylate were dissolved in 49.0 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 μm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained as described in Example 2. The refractive index was found to be 1.806 and the absorption parameter was 0.58. The film thickness loss of the antireflective coating when baked at 200°C for 60 seconds and soaked in propylene glycol monomethyl ether acetate (PGMEA) for 60 seconds was found to be 0%. The performance of the anti-reflective coating formulation was evaluated using the photoresist of Example 1. About 40 nm thick film was coated and baked at 200°C for 60 seconds on a silicon wafer with the anti-reflective coating formulation of this Example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C for 60 seconds. The wafer was then imagewise exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqueous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Example 14

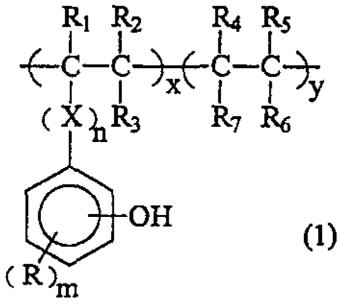
53.4 g (0.3 mol) of o-hydroxyphenyl methacrylate was dissolved in 80.1 g of dry tetrahydrofuran and to this solution was added 5.34 g of 2,2'-azobisisobutyronitrile (AIBN). The contents were stirred at 70°C under nitrogen atmosphere for 5 hours. The viscous solution was poured in to isopropanol and the precipitate washed and re-precipitated two more times in isopropanol. Thus 40 g of polymer was isolated, dried under vacuum.

Example 15

An antireflective coating composition was made by dissolving 1.0 g of poly(2-hydroxyphenyl methacrylate) prepared in Example 14 and 0.294 g of tetrakis(methoxymethyl)glycoluril (Powderlink® available from Cytec Industries, West Paterson, New Jersey), 0.013 g of p-nitrobenzyl tosylate were dissolved in 49 g of ethyl lactate. The solution was filtered through 0.45 and 0.2 μm filters. The n (refractive index) and k (absorption parameter) of the antireflective coating were obtained by baking a silicon wafer coated with the antireflective composition at a temperature of 220°C for 60 seconds and measuring the n and k values with an ellipsometer at 193 nm. The refractive index was found to be 1.8087 and the absorption parameter was 0.652. About 40 nm thick film was coated on a silicon wafer with the anti-reflective coating formulation of this example. Then a 500 nm thick photoresist solution from Example 1 was coated and baked at 115°C. The wafer was then exposed using a 193 nm exposure tool. The exposed wafer was baked at 110°C for 60 seconds and developed using a 2.38 wt % aqeous solution of tetramethyl ammonium hydroxide for 60 seconds. The line and space patterns when observed under scanning electron microscope showed no standing waves indicating the efficacy of the bottom anti-reflective coating.

Claims

1. A composition which is useful for forming an antireflective coating for a photoresist, comprising a polymer with the structure



(1)

where,

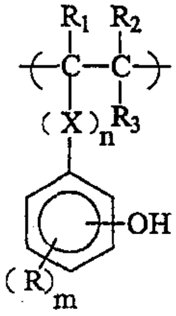
X is CO_2, O or SO_2 and n=0 or 1, x is an integer and y is 0 or an integer, providing when n=0, y is an integer,

R is hydrogen, halogen, nitro, alkyl(C_1-C_4), alkoxy(C_1-C_4) or esters(C_1-C_4), and, m=1-4,

R_1 to R_7 are independently hydrogen, halogen, alkyl(C_1-C_4), alicyclic group, alkoxy(C_1-C_4), esters(C_1-C_4), CO_2 (alkyl)OH, CO_2(alkyl)$COCH_2COCH_3$, further where R_7 and R_6 are combined to form a saturated ring or anhydride,

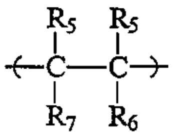
a crosslinker, a thermal acid generator and a solvent.

2. The composition of claim 1, where the polymer comprises at least one recurring phenolic unit with the structure (2)



(2)

and at least one recurring nonaromatic unit with the structure



$$\leftarrow \overset{R_5}{\underset{R_7}{C}} - \overset{R_5}{\underset{R_6}{C}} \rightarrow \quad (3)$$

where,

X is CO_2, O or SO_2 and n=0 or 1,

R is hydrogen, halogen, nitro, alkyl(C_1-C_4), alkoxy(C_1-C_4) or esters(C_1-C_4), and, m=1-4,

R_1 to R_7 are independently hydrogen, halogen, alkyl(C_1-C_4), alicyclic group, alkoxy(C_1-C_4), esters(C_1-C_4), CO_2 (alkyl)OH, CO_2(alkyl)$COCH_2COCH_3$, further where R_7 and R_6 are combined to form a saturated ring or anhydride.

3. The composition of claim 1, where the absorption parameter (k) of the antireflective coating is between 0.3 and 0.7 at the wavelength at which the photoresist is sensitive.

4. The composition of claim 2, where the nonaromatic unit constitutes at least about 35 mole % of the copolymer.

5. The composition of claim 1, where the crosslinker is selected from melamines, methylols, glycolurils, hydroxy alkyl amides, epoxy and epoxy amine resins, blocked isocyanates, and divinyl monomers.

6. The composition of claim 1, where the thermal acid generator is selected from nitrobenzyl tosylates, nitrobenzyl benzenesulfonates and phenolic sulfonates.

7. The composition of claim 1, where the thermal acid generator is activated at above 90°C.

8. The composition of claim 1, where the thermal acid generator is activated at above 150°C.

9. The composition of claim 1, where the thermal acid generator is activated at above190°C.

10. The composition of claim 1, where the solvent is selected from propylene gycol monomethyl ether acetate, propylene gycol monomethyl ether, and ethyl lactate, 2-heptanone, cyclopentanone, cyclohexanone, and gamma butyrolactone.

11. The composition of claim 1, where the polymer is selected from poly(hydroxystyrene-methyl methacrylate), poly(hydroxyphenyl methacrylate- methyl methacrylate), poly(hydroxyphenyl methacrylate) or mixtures thereof.

12. The composition of claim 1, where the photoresist is sensitive to wavelengths between 130 nm to 220 nm.

13. The composition of claim 1, where the photoresist comprises a non-aromatic polymer, a photoactive compound and a photoresist solvent.

14. The composition of claim 1, where the composition further comprises other polymers selected from polyhydroxystyrene, novolak, polyarylate and polymethylmethacrylate.

15. The composition of claim 14, where the amount of other polymer is less than 50 weight % of the total solids.

16. The composition of claim 1, where the composition further comprises additives selected from leveling agents, dyes and adhesion promoter.

17. An article comprising a substrate with a layer of antireflective coating composition of claim 1 and thereon a coating of photoresist comprising a non-aromatic polymer, a photoactive compound and a photoresist solvent.

18. A process for forming an image comprising,
   a) coating and baking a substrate with the antireflective coating composition of claim1;
   b) coating and baking a photoresist film on top of the antireflective coating;
   c) imagewise exposing the photoresist;
   d) developing an image in the photoresist;
   e) optionally, baking the substrate after the exposing step.

19. The process of claim 18, where the photoresist is imagewise exposed at wavelengths between 130 nm to 220 nm.

20. The process of claim 18, where the photoresist comprises a non-aromatic polymer, a photoactive compound and a photoresist solvent.

21. The process of claim 18, where the antireflective coating is baked at temperatures greater than 90°C.

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权利要求书4页 说明书19页 附图页数0页

[54]发明名称 用于深紫外线光刻胶的防反射组合物

[57]摘要

本发明涉及一种新颖的防反射涂料组合物，其中该组合物包括共聚物、热酸产生剂和溶剂组合物。本发明进一步包括将该组合物用于光刻的方法。该组合物强有力地吸收约130nm至约250nm的辐射。

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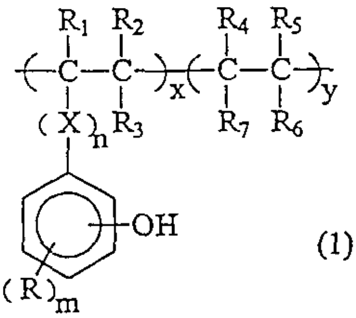
权 利 要 求 书

1. 一种可用于对光刻胶形成防反射涂层的组合物，包括具有如下结构的聚合物：



(1)

其中：

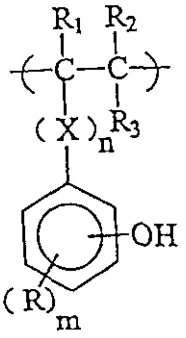
X 为 CO_2、O 或 SO_2 和 n=0 或 1，x 为整数，以及 y 为 0 或整数，条件是当 n=0 时，y 为整数，

R 为氢、卤素、硝基、烷基（C_1-C_4）、烷氧基（C_1-C_4）或酯（C_1-C_4），以及 m=1-4，

R_1 至 R_7 独立地为氢、卤素、烷基（C_1-C_4）、脂环基团、烷氧基（C_1-C_4）、酯（C_1-C_4）、CO_2(烷基)OH、CO_2(烷基)$COCH_2COCH_3$，还有其中 R_7 和 R_6 结合形成饱和环或酸酐，

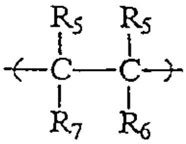
交联剂、热酸产生剂和溶剂。

2. 权利要求 1 的组合物，其中所述聚合物包含至少一种具有如下结构(2) 的重复酚单元



(2)

和至少一种具有如下结构(3)的重复非芳烃单元



$$-\left(\underset{R_7}{\overset{R_5}{C}}-\underset{R_6}{\overset{R_5}{C}}\right)- \quad (3)$$

其中:

X 为 CO_2、0 或 SO_2 和 n=0 或 1,

R 为氢、卤素、硝基、烷基(C_1-C_4)、烷氧基(C_1-C_4) 或酯(C_1-C_4),以及 m=1-4,

R_1 至 R_7 独立地为氢、卤素、烷基(C_1-C_4)、脂环基团、烷氧基(C_1-C_4)、酯(C_1-C_4)、CO_2(烷基)OH、CO_2(烷基)$COCH_2COCH_3$,还有其中 R_7 和 R_6 结合形成饱和环或酸酐。

3. 权利要求 1 的组合物,其中所述防反射涂料的吸收参数(k)在光刻胶敏感的波长处为 0.3 至 0.7。

4. 权利要求 2 的组合物,其中所述非芳烃单元构成该共聚物的至少约 35 mol%。

5. 权利要求 1 的组合物,其中所述交联剂选自三聚氰胺类、羟甲基化物、甘脲类、羟烷基酰胺类、环氧和环氧胺树脂类、封闭异氰酸酯类、和二乙烯基单体类。

6. 权利要求 1 的组合物,其中所述热酸产生剂选自甲苯磺酸硝基苄基酯类、苯磺酸硝基苄基酯类和酚磺酸酯类。

7. 权利要求 1 的组合物,其中所述热酸产生剂在高于 90 下活化。

8. 权利要求 1 的组合物,其中所述热酸产生剂在高于 150 下活化。

9. 权利要求 1 的组合物,其中所述热酸产生剂在高于 190 下活

化。

10. 权利要求1的组合物，其中所述溶剂选自丙二醇单甲醚乙酸酯、丙二醇单甲醚、乳酸乙酯、2-庚酮、环戊酮、环己酮和γ-丁内酯。

11. 权利要求1的组合物，其中所述聚合物选自聚(羟基苯乙烯-甲基丙烯酸甲酯)、聚(甲基丙烯酸羟苯基酯-甲基丙烯酸甲酯)、聚(甲基丙烯酸羟苯基酯)或其混合物。

12. 权利要求1的组合物，其中所述光刻胶对130至220 nm波长敏感。

13. 权利要求1的组合物，其中所述光刻胶包括非芳烃聚合物、光活性化合物和光刻胶溶剂。

14. 权利要求1的组合物，其中所述组合物进一步包括选自聚羟基苯乙烯、线型酚醛树脂、聚丙烯酸酯和聚甲基丙烯酸甲酯的其它聚合物。

15. 权利要求14的组合物，其中其它聚合物的量低于总固体的50 wt%。

16. 权利要求1的组合物，其中该组合物还包括选自流平剂、染料和增粘剂的添加剂。

17. 一种制品，包括具有权利要求1的防反射涂料组合物层以及在该层上具有包括非芳族聚合物、光活性化合物和光刻胶溶剂的光刻胶涂层的衬底。

18. 一种形成图形的方法，包括：

a) 用权利要求1的反射涂料组合物涂布衬底并烘烤；

b) 在防反射涂层上涂布光刻胶薄膜并烘烤；

c) 对该光刻胶进行成像曝光；

d) 对该光刻胶进行显影；和

e) 可任选地在曝光后烘烤衬底。

19. 权利要求18的方法，其中将光刻胶在130 nm至约200 nm的波长下进行成像曝光。

20. 权利要求18的方法，其中所述光刻胶包括非芳族聚合物、光

活性化合物和光刻胶溶剂。

21. 权利要求 18 的方法，其中将该防反射涂层高于 90℃ 的温度下烘烤。

说　明　书

用于深紫外线光刻胶的防反射组合物

背景技术

本发明涉及新的防反射涂料组合物和用于通过在反射衬底（substrate）与光刻胶涂层之间形成该新防反射涂料组合物薄层进行图像处理中的用途。此类组合物特别适用于通过用光刻（photolithographic）技术加工半导体元件，尤其是需要用深紫外线曝光的那些半导体元件。

光刻胶组合物用于微光刻（microlithography）工艺中制造微型化电子部件，例如制造计算机芯片和集成电路。在这些方法中，通常首先将光刻胶组合物薄涂膜施于衬底，如用于制造集成电路的硅片上。然后将该涂布的衬底烘烤以蒸发光刻胶组合物中的所有溶剂并使涂层固定在衬底上。接着将衬底的经烘烤涂布表面在辐射下进行成像曝光。

这种辐射曝光在涂布表面的曝光区域造成化学变化。可见光、紫外光、电子束和 X-射线辐射能是目前常用于微光刻工艺中辐射类型。在这种成像曝光后，将涂布衬底用显影溶液处理以溶解并除去辐射暴光或未暴光区域的光刻胶。

半导体元件微型化的趋势导致采用对越来越低波长辐射敏感的新型光刻胶，且还导致使用复杂的多层体系以克服与此微型化有关的问题。

对于构成低于四分之一微米几何尺寸的图形化成像，可利用高分辨的化学增强深紫外线(100-300 nm)正和负色调光刻胶。有两种主要的深紫外线(UV)曝光技术提供对微型化明显的改进，它们是在 248 nm 和 193 nm 处发出辐射的激光。此类光刻胶的例子在 US 4,491,628、US 5,350,660、EP794458 和 GB 2320718 中给出，这些专利这里作为参考引入。用于 248 nm 的光刻胶通常基于取代的聚羟基苯乙烯和其共

聚物。另一方面，用于193 nm曝光的光刻胶需要非芳族聚合物，因为芳烃在此波长下不透明。通常将脂环族烃加入聚合物中以弥补不存在芳烃造成的耐蚀刻损失。此外，在较低波长下，来自衬底的反射更加剧对光刻胶的光刻性能的损害。因此，在这些波长下，防反射涂料变得至关重要。

将高吸收性防反射涂料用于光刻中是消除光从高反射衬底反射回来造成的问题的一个较简单方法。回反射性的两个主要缺点是薄薄膜的干涉影响和反射刻痕。随着光刻胶厚度变化，薄薄膜干涉或驻波导致临界线宽度尺寸变化，此变化是光刻胶薄膜中的总光强度变化造成的。当光刻胶在包括分布（topographic）特征的衬底上构图时，反射刻痕将变得严重，包括分布特征的衬底通过光刻胶膜散射光，导致线宽变化，在极端情况下，形成光刻胶完全损失的区域。

过去将染色光刻胶用于解决这些反射问题。然而，通常已知，染色光刻胶仅降低来自衬底的反射，但不能完全消除此反射。此外，染色光刻胶还造成光刻胶的光刻性能降低，以及染料可能升华和染料在光刻胶薄膜中不完全相容。

当需要进一步降低或消除线宽变化时，使用底部防反射涂料提供了消除反射的最佳解决方法。在用光刻胶涂布和曝光前将底部防反射涂料施于衬底上。将光刻胶曝光成像并显影。然后通常在氧等离子体中将曝光区域中的防反射涂料蚀刻，从而将抗蚀图转移到衬底上。防反射薄膜的蚀刻速率应比光刻胶相对高一些，这样在蚀刻工艺期间不过分损失光刻胶薄膜的条件下蚀刻防反射薄膜，无机类防反射涂层包括诸如TiN、TiON、TiW和其上旋涂有30 NM范围的机聚合物的薄膜，并描述于如下论文中：C. Nolscher等人，Proc SPIE第1086卷，242页（1989）；K. Bather, H. Schreiber,《薄固体膜》（Thin solid films），200，93，（1991）；G. Czech等人，《微电子工程》（Microelectronic Engineering），21，51页（1993）。无机B. A. R. C要求精确控制薄膜厚度、薄膜均匀性、特殊的沉积装置、光刻胶涂布前的复杂增粘技术、分开的干燥蚀刻图形转移步骤、和用于除去的干

蚀刻。

有机 B.A.R.C 是更优选的，并通过将染料加入聚合物涂料中配制（Proc SPIE 第 1086 卷，(1989),106 页）。这种掺混染料的涂料的问题包括 1)在旋涂期间聚合物与染料组分的分离问题，2)染料汽提入光刻胶溶剂中，和 3)在烘烤工艺中热扩散入光刻胶中。这些影响造成光刻胶性能降解，因此不是优选的组合物。

光吸收成膜聚合物是另一种选择。聚合物有机防反射涂料是本领域已知的，如 EP 583,205 中描述的，该文献这里作为参考引入。然而，EP 583,205 中描述的防反射薄膜自有机溶剂如环己酮和环戊酮流延。使用此类有机溶剂操作的潜在危险性已导致开发防反射涂料组合物，如 US 5,652,317 中公开的那些，其中防反射涂料的固体组分是可溶的并且可由低毒危险性的溶剂旋涂流延。半导体工业中已知的具有低毒性的优选溶剂是丙二醇单甲基醚乙酸酯(PGMEA)、丙二醇单甲基醚(PGME)和乳酸乙酯。使用可溶于优选的低毒性溶剂的防反射涂料的另一优点是，这些相同的溶剂还可用于除去防反射涂料的边缘珠粒，且不会出现另外的危险或装置费用，因为这些溶剂还用于光刻胶和光刻胶加工中。现有技术中公开的本发明聚合物构成这样一些聚合物，即其中生色团为来自聚合物主链的侧基，和其中通常为芳烃的生色团在光刻胶曝光的波长如 436 nm、365 nm 和 248 nm 下吸收。已发现这些聚合物用作对 193 nm 敏感的光刻胶的防反射涂料时无效。据信，这些防反射聚合物芳烃性能特别突出，因此反射性太强，从而起到的是镜面而非吸收剂的作用。此外，由于这些聚合物为高度芳烃的，与用于 193 nm 曝光的新型非芳烃光刻胶相比具有太低的干燥蚀刻速率，因此对成像和蚀刻无效。若防反射涂料的干燥蚀刻速率类似于或低于涂于防反射涂层上面的光刻胶的蚀刻速率，则光刻胶图形会被损害或不能准确转移至衬底上。

EP 542 008 中公开的防反射组合物基于高级芳族聚合物，如线型酚醛树脂、聚乙烯基苯酚、聚乙烯基苯酚与苯乙烯或α-甲基苯乙烯的共聚物等。此外，这种防反射涂料必须能够与光刻胶交联，其中光刻

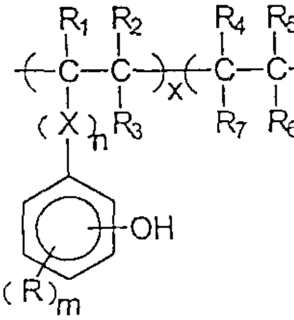
胶基于在 248 nm 处敏感的聚乙烯基苯酚树脂。然而，防反射涂料和光刻胶中的高芳烃程度以及线型酚醛树脂、聚乙烯基苯酚等的低蚀刻速度对在 193 nm 处的成像加工有害。因此，必须具有在曝光低于 230 NM 时充分起作用的底部防反射涂料。

已发现，本发明的新颖防反射涂料具有能够使图像完整转移至衬底上的良好干燥蚀刻性能，和良好的吸收特性以防止特别是在 193 nm 处的反射蚀刻和线宽变化或驻波。此外，在防反射涂料与光刻胶薄膜之间基本上不存在混合。这些防反射涂料还具有良好的溶液稳定性，且特别可形成具有良好涂层质量的薄膜，后者对于光刻是特别有利的。当将防反射涂料与光刻胶一起用于成像工艺中时，可获得清洁的图像。

本发明概述

本发明涉及适用于与光刻胶一起使用的新颖防反射涂料组合物，其中该组合物包括共聚物、热酸产生剂和溶剂组合物。本发明进一步包括将该组合物用于光刻的方法。该组合物强有力地吸收约 130 nm 至约 250 nm 的辐射。

该新颖组合物的聚合物具有如下结构：



(1)

其中：

X 为 CO_2、O 或 SO_2和 n=0 或 1，x 为整数，以及 y 为 0 或整数，条件是当 n=0 时，y 为整数。

R 为氢、卤素、硝基、烷基(C_1-C_4)、烷氧基(C_1-C_4)或酯(C_1-C_4)，以及 m=1-4，

R_1 至 R_7 独立地为氢、卤素、烷基(C_1-C_4)、脂环基团、烷氧基(C_1-C_4)、酯(C_1-C_4)、CO_2(烷基)OH、CO_2(烷基)$COCH_2COCH_3$，还有其中 R_7 和 R_6 结合形成饱和环或酸酐。

这些聚合物优选为聚(羟基苯乙烯-甲基丙烯酸甲酯)、聚(甲基丙烯酸羟苯基酯-甲基丙烯酸甲酯)、聚(甲基丙烯酸羟苯基酯)或其混合物。

热酸产生剂在高于 90℃，优选高于 150℃，更优选高于 190℃下活化。

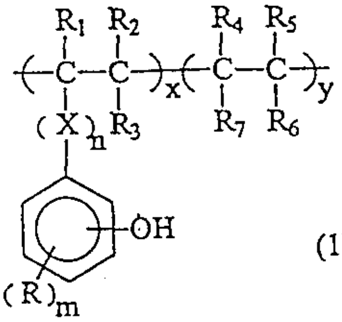
该新颖组合物的溶剂为有机溶剂，特别是低毒并且还具有良好涂布和溶解性能的溶剂。公知的具有低毒并可用于溶解本发明组合物固体组分的优选有机溶剂为丙二醇单甲醚乙酸酯(PGMEA)、丙二醇单甲醚(PGME)、乳酸乙酯(EL)和 2-庚酮，不过还可单独或以混合物形式使用其它低毒溶剂。

本发明还涉及一种制品，它包括具有所述新颖防反射涂料组合物层以及在该层上具有包括非芳族聚合物、光活性化合物和光刻胶溶剂的光刻胶涂层的衬底。

本发明进一步包括在衬底上形成图形的方法。将该衬底涂布本发明防反射涂料膜，将其加热以除去所有残余溶剂并使涂层不溶解。然后在该防反射涂层上面由光刻胶溶液形成薄膜并进一步加热以基本除去光刻胶溶剂。将该光刻胶薄膜（优选包括在 193 nm 处敏感的非芳烃聚合物）通过光掩模在约 130 nm 至约 300 m 的紫外线辐射下进行成像曝光，并在显影剂中处理以呈现光刻胶图形。该光刻胶优选包括非芳烃聚合物、光活性化合物和光刻胶溶剂。可将该衬底在显影步骤之前或之后加热，以得到质量优异的图像。然后可将该经曝光的薄膜通常在含氧气的等离子体中干燥蚀刻，其中光刻胶图形起到蚀刻光掩模的作用。

本发明详细描述

本发明涉及一种新颖防反射涂料组合物，其中该组合物包括聚合物、交联剂、热酸产生剂和溶剂成分。本发明进一步包括将该组合物用于光刻的方法。该新颖组合物的聚合物具有如下结构：



(1)

其中：

X 为 CO_2、O 或 SO_2 和 n=0 或 1，x 为整数，以及 y 为 0 或整数，条件是当 n=0 时，y 为整数。

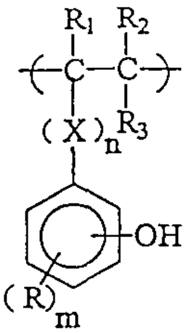
R 为氢、卤素、硝基、烷基 (C_1-C_4)、烷氧基 (C_1-C_4) 或酯 (C_1-C_4)，以及 m=1-4，

R_1 至 R_7 独立地为氢、卤素、烷基 (C_1-C_4)、脂环基团、烷氧基 (C_1-C_4)、酯 (C_1-C_4)、CO_2(烷基)OH、 CO_2(烷基)$COCH_2COCH_3$，还有其中 R_7 和 R_6 结合形成饱和环或酸酐。

该聚合物对吸收深紫外区，尤其是约 193 nm 处的辐射特别有效。

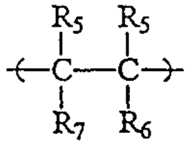
本发明的聚合物可为仅有酚单元的均聚物，其中 X 表示 CO_2、O 或 SO_2，n=0 和 y = 0。该均聚物的一个例子是聚(甲基丙烯酸羟苯基酯)。本发明排除聚羟基苯乙烯或线型酚醛树脂作为主聚合物组分。

本发明聚合物还可包括含至少一种具有如下结构 (2) 的重复酚单元



(2)

和至少一种具有如下结构(3)的重复非芳烃单元的共聚物。



$$-\!\!\left(\overset{R_5}{\underset{R_7}{C}}-\overset{R_5}{\underset{R_6}{C}}\right)\!\!-$$

(3)

酚单元提供交联点以及在深 UV 区吸收的生色团。该羟基优选处于邻位或对位，更优选处于对位。其它取代基也可存在于芳环上，只要它们不为芳烃且不含将导致在长紫外区即 320 nm 至 450 nm 吸收的任何共轭基团即可。与苯酚共轭的取代基如-N=N-或-C=C-将被排除。芳环的取代基优选为氢、烷基、烷氧基、酯、硝基或卤素；例子是甲基、乙基、丙基、异丙基、丁基、叔丁基、甲氧基、乙氧基、丙氧基、丁氧基、乙酰氧基和氯，更优选氢、硝基或烷基。苯酚可直接或通过连接基团 X 与主链连接，其中 X 为 CO_2、SO_2或 O，优选 CO_2。该共聚物可包括单一类型的苯酚单元，或两类或多类苯酚单元的混合物，取决于所需的防反射涂料的特性。不同的取代基可用于增强某些性能，例如粘结力、溶解性能、吸收性能和成膜性能。用于与非芳烃单体聚合的优选酚单体为羟基苯乙烯、甲基丙烯酸羟苯基酯、或其混合物。

非芳烃单元可为不含芳基的任何不饱和单元。用于聚合的共聚单体的具体例子是丙烯酸或甲基丙烯酸、丙烯酸酯、甲基丙烯酸酯、马来酸酐、丙烯腈、乙烯基醚等。可使用一种非芳烃共聚单体或两种或多种非芳烃共聚单体的混合物，取决于所需的防反射涂料的特性。不同的取代基可用于增强例如粘结力、溶解性能、吸收性能和成膜性能。

酚单元与非芳烃单元在共聚物中的比例可根据防反射涂料所需的性能而变化，酚单元优选为约 35 mol％至约 65 mol％，更优选约 45 mol

%至约 55 mol%，特别是其中羟基苯乙烯或其衍生物用作酚单体时。

该新颖组合物在 193 nm 处的吸收参数(k)为约 0.3 至约 0.7，优选约 0.5 至约 0.65，用椭圆测量计（ellipsometry）测量。折光率数值(n)为约 1.25 至约 1.9。由于该组合物在 193 nm 处的良好吸收特性，可使用大小约 40 nm 的极薄防反射薄膜。当使用非芳烃光刻胶如在 193 nm 处敏感的那些非芳烃光刻胶时，若该光刻胶薄膜薄且必须起到防反射薄膜的蚀刻光掩模作用，则这是特别有利的。防反射涂料的薄膜厚度低于 150 nm，更优选低于 90 nm。

本发明聚合物可按本领域已知的任何标准聚合方法制备，这些方法的例子是自由基、阴离子或阳离子共聚技术。聚合物可用溶液、乳液、本体、悬浮聚合等合成。该聚合物还可由封端单体合成，例如其中在聚合前将酚单体的羟基基团用诸如乙酰基基团封闭，在聚合物合成后将该封闭基团水解，由此得到本发明新颖组合物的聚合物。该共聚物可具有各种结构，如无规、嵌段、接枝等。聚合物的重均分子量可为约 1500 至约 50,000，优选 4,000 至约 30,000，更优选 5,000 至约 20,000。当重均分子量低于 1,500 时，对于防反射涂料不能获得良好的成膜性能，当重均分子量太高时，则会损害诸如溶解性、贮存稳定性等。

各种交联剂可用于本发明组合物中。可使用在酸存在下可交联聚合物的任何合适交联剂。这些交联剂的例子是三聚氰胺类、羟甲基化物（methyols）、甘脲类、羟烷基酰胺类、环氧和环氧胺树脂类、封闭异氰酸酯类、和二乙烯基单体类。优选三聚氰胺类如六甲氧基甲基三聚氰胺、甘脲类如四(甲氧基甲基）甘脲、和芳烃羟甲基类如 2,6-双羟甲基对甲酚。

本发明的热酸产生剂为加热至温度高于 90℃和低于 250℃时产生酸的化合物。该酸与交联剂一起交联聚合物。防反射薄膜热处理后变为不溶于用于涂布光刻胶的溶剂中，而且也不溶于用于使光刻胶成像的碱性显影剂中。热酸产生剂优选在 90℃，更优选在 150℃，进一步更优选在 190℃下活化。将防反射薄膜加热足够长时间以使涂料交

联。热酸产生剂的例子是甲苯磺酸硝基苄基酯如甲苯磺酸2-硝基苄基酯、甲苯磺酸2,4-二硝基苄基酯、甲苯磺酸2,6-二硝基苄基酯、甲苯磺酸4-硝基苄基酯；苯磺酸硝基苄基酯如4-氯苯磺酸2-三氟甲基-6-硝基苄基酯、4-硝基苯磺酸2-三氟甲基-6-硝基苄基酯；酚磺酸酯如4-甲氧基苯磺酸苯基酯。

在该新颖防反射组合物中，热酸产生剂优于游离酸，尽管也可以使用游离酸，因为随着时间的流逝防反射溶液的贮存稳定性可因酸的存在而受到影响。只有当加热在衬底上的防反射薄膜时才活化热酸产生剂。尽管热酸产生剂对于有效交联聚合物是优选的，但也可以使用包括聚合物和交联剂的防反射组合物，其中加热交联聚合物。

共聚物在本发明组合物中的量可为约90 wt%至约50 wt%，优选约85 wt%至约70 wt%，更优选约80 wt%至约70 wt%，按组合物的固体部分计。交联剂在本发明组合物中的量可为约5 wt%至约50 wt%，优选约15 wt%至约30 wt%，按组合物的固体部分计。热酸产生剂在本发明组合物中的量可为约0.1 wt%至约5 wt%，优选约0.5 wt%至约3 wt%，更优选约1 wt%至约2 wt%，按组合物的固体部分计。

可用于本发明组合物的典型溶剂（单一溶剂或混合物）为丙二醇单甲醚乙酸酯(PGMEA)、丙二醇单甲醚(PGME)和乳酸乙酯(EL)、2-庚酮、环戊酮、环己酮和γ-丁内酯，但优选PGME、PGMEA和EL或其混合物。具有低毒性、良好涂覆性和溶解性的溶剂通常是优选的。

防反射涂料组合物包括本发明的共聚物、交联剂和热酸产生剂以及合适的溶剂或溶剂混合物。为增强涂料的性能可加入其它组分如单体染料、低级醇、表面流平剂、增粘剂、消泡剂等。其它聚合物如线型酚醛树脂、聚羟基苯乙烯、聚甲基丙烯酸甲酯和聚丙烯酸酯可加入组合物中，条件是对性能无不利影响。优选将这种聚合物的量保持低于组合物总固体的50 wt%，更优选20 wt%，进一步更优选低于10 wt%。

由于防反射薄膜被涂覆于衬底的上面并要进一步进行干燥蚀刻，

因此可预想该薄膜应具有足够低的金属离子含量和足够纯度，这样对半导体的性能才会没有不利影响。进行处理如将聚合物的溶液通过离子交换柱、过滤和萃取方法可降低金属离子的浓度和减少颗粒。

该防反射涂料组合物可用本领域公知的技术如浸涂、旋涂或喷涂涂覆于衬底上。防反射涂层的膜厚度为约 20 nm 至约 200 nm。正如本领域所公知的那样，最佳薄膜厚度为在光刻胶中观察不到驻波时的厚度。已意想不到地发现，对于此新颖组合物，可使用极薄的涂层，原因在于该薄膜具有优良的吸收和折射率性能。将该薄膜进一步在热板或对流烘箱上加热足够长的时间，以除去任何残留的溶剂并诱导交联，使防反射涂层不溶解以防止防反射涂层与光刻胶层混合。

光刻胶可为用于半导体工业的任何类型的光刻胶，只要光刻胶和防反射涂料中的光活化物质在用于成像处理的曝光波长下吸收即可。

存在两类光刻胶组合物：负工作（negative-working）和正工作（positive-working）光刻胶组合物。当负工作光刻胶组合物进行辐射成像曝光时，暴露于辐射的光刻胶组合物区域变得较不溶于显影剂溶液（如发生交联反应），而未曝光的光刻胶涂层区域保持相对溶于该溶液。这样，用显影剂处理已曝光的负工作光刻胶导致除去光刻胶涂层的未曝光区域并在涂层中形成负图像，由此暴露其上沉积有光刻胶组合物的下面衬底表面的所需部分。

另一方面，当正工作光刻胶组合物进行辐射成像曝光时，那些暴露于辐射的光刻胶组合物区域变得更溶于显影剂溶液（如发生重排反应），而未曝光的涂层区域保持相对不溶于该溶液。这样，用显影剂处理已曝光的正工作光刻胶导致除去涂层的已曝光区域并在光刻胶涂层中形成正图像。同样暴露下面表面的所需部分。

正工作光刻胶组合物目前比负工作光刻胶更受青睐，原因在于前者通常具有更好的图形分辨性能和图形转移特性。图形分辨性定义为光刻胶组合物在曝光和显影后可以高的图像边缘分辨力从光掩模转移至衬底上的最小特征。在目前的很多制造应用中，要求光刻胶的图形分辨率数量级低于 1 μm。此外，几乎总是要求已显影的光刻胶壁轮廓

线接近垂直于衬底。光刻胶涂层的显影与未显影区域的这种分界转化为光掩模图像在衬底上的精确图形转移。随着微型化发展趋势降低了元件的临界尺寸，这变得更为重要。

当要求亚半微米（subhalfmicron）几何尺寸时，也可使用对约130 nm 至约 250 nm 之间的短波长光敏感的光刻胶。特别优选包括非芳烃聚合物、光致酸产生剂、可有可无的溶解抑制剂和溶剂的光刻胶。本领域已知的在 193 nm 处敏感的光刻胶描述于 EP 794458、WO 97/33198 和 US 5,585,219 中，这些文献这里作为参考引入。不过可将在 193 nm 处敏感的任何光刻胶涂覆于本发明防反射组合物上面。

本发明方法还包括用该新颖防反射涂料涂布衬底，并在热板或对流烘箱上在足够高温度下加热足够长时间以除去涂料溶剂，并将该聚合物交联至足够的程度使涂层不溶于光刻胶涂料溶液或含水碱性显影剂。可用本领域公知的方法使用边缘珠粒除去器清洁衬底边缘。温度的优选范围为约 90℃ 至约 250℃。若温度低于 90℃，则发生溶剂除去不足或交联量不足，而当温度高于 250℃ 时，组合物会变得化学不稳定。然后将光刻胶涂于防反射涂层上面，并烘烤以基本上除去光刻胶溶剂。将该光刻胶进行成像曝光并在显影剂水溶液中显影以除去已处理的光刻胶。该显影剂优选为包括例如氢氧化四甲基铵的含水碱性溶液。在显影之前和曝光后可将一非必需的加热步骤引入方法中。光刻胶涂布和成像方法是本领域公知的并根据使用的具体类型的光刻胶优化。然后可将已图形化的衬底在合适的蚀刻槽中干燥蚀刻以除去防反射膜的曝光部分，其中残余的光刻胶起到蚀刻光掩模的作用。

可在防反射涂层与光刻胶之间设置一中间层以防止掺混，并且这一点也可想象是在本发明范围内。中间层为由溶剂流延的惰性聚合物，其中聚合物的例子为聚砜和聚酰亚胺。

下面的具体实施例提供对生产和使用本发明组合物的方法的详细描述。然而，这些实施例不以任何方式限制范围，且不应认为是提供为实施本发明必须唯一使用的条件、参数和数值。

实施例 1

用 3.311 g 甲羟戊酸内酯甲基丙烯酸酯与甲基丙烯酸 2-甲基金刚烷基酯的共聚物、0.1361 g 九氟-1-丁磺酸二苯基碘鎓、0.00265 g 哌啶乙醇和 20 g 乳酸乙酯配制用于涂覆在本发明防反射涂层上面的光刻胶。将该溶液用 0.45 和 0.2 μm 过滤器过滤。涂布 500 nm 厚的光刻胶溶液并在 115℃下烘烤 60 秒。然后将该基片用 193 nm 的曝光工具进行成像曝光。将已曝光的基片在 110℃下烘烤 60 秒并用氢氧化四甲基铵的 2.38 wt% 水溶液显影 60 秒。在扫描电子显微镜下观察，线路和间隔图形显示不可接受的驻波。

实施例 2（比较例）

通过将 1.0 g 聚(4-羟基苯乙烯)、0.299 g 四(甲氧基甲基)甘脲（Powderlink ®，购自 Cytec Industries，West Paterson，New Jersey）、0.013 g 甲苯磺酸对硝基苄基酯溶于 49.0 g 乳酸乙酯中，制备防反射涂料组合物。将该溶液通过 0.45 和 0.2 μm 过滤器过滤。通过将涂有防反射组合物的硅片在 220℃温度下烘烤 60 秒，然后通过在 J.A. Woollam®VASE 分光镜椭圆测量仪上在 185 至 1000 nm 范围内进行分光镜椭圆测量分析，获得防反射涂料的 n 值（折射率）和 k 值（吸收参数）。在 6 个入射角（55-80°，每步间隔 5°）下在 450 个波长处收集数据，得到超过 2500 个单独的椭圆测量仪测定值。所有测量值使用动态平均。动态平均适用于其中灯输出量大大减少的 DUV 范围。

首先在波长>400 nm 下分析薄膜，假定薄膜为纯介电性的（即透明的）。此分析可确定人们未知的薄膜厚度，以及一组描述长波长范围的折射率 n 的真实部分的 Cauchy 系数。然后通过从早先分析已知的薄膜厚度，在各波长下分析该数据，对于各薄膜得到一组分散的曲线 n（折射率）和 k（吸收参数）。使用此方法分析各薄膜。发现折射率为 1.73，吸收参数为 0.9013。

用实施例 1 的光刻胶评估防反射涂料配方的性能。在硅片上用本

实施例的防反射涂料配方涂布约 40 nm 厚的薄膜，并在 200℃下烘烤 60 秒。然后涂布 500 nm 厚的实施例 1 的光刻胶溶液并在 115℃下烘烤。然后将该基片用 193 nm 的曝光工具进行成像曝光。将已曝光的基片在 110℃下烘烤 60 秒并用氢氧化四甲基铵的 2.38 wt% 水溶液显影 60 秒。在光刻胶图像中观察到驻波。

实施例 3

通过将 6 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚物、1.8 g 2,6-双羟甲基对甲酚和 0.078 g 对甲苯磺酸一水合物溶于 48 g 乳酸乙酯与丙二醇单甲基醚乙酸酯的 1:1 混合物中，制备防反射涂料组合物。将该溶液通过 0.45 和 0.2 μm 过滤器过滤。按实施例 2 所述获得该防反射涂料的 n（折射率）和 k（吸收参数）。测得折射率为 1.466，吸收参数为 0.576。在 200℃下烘烤 60 秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡 60 秒后测得薄膜厚度损失低于 1.8%。用实施例 1 的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约 40 nm 厚的薄膜，并在 200℃下烘烤 60 秒。然后涂布 500 nm 厚的实施例 1 的光刻胶溶液并在 115℃下烘烤 60 秒。然后将该基片用 193 nm 的曝光工具进行成像曝光。将已曝光的基片在 110℃下烘烤 60 秒并用氢氧化四甲基铵的 2.38 wt% 水溶液显影 60 秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例 4

通过将 3 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚物、0.9 g 2,6-双羟甲基对甲酚和 0.0039 g 对甲苯磺酸一水合物溶于 27 g 乳酸乙酯中，制备防反射涂料组合物。将该溶液通过 0.45 和 0.2 μm 过滤器过滤。按实施例 2 所述获得该防反射涂料的 n（折射率）和 k（吸收参数）。测得折射率为 1.466，吸收参数为 0.576。在 200℃下烘烤 60 秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡 60 秒后测得薄膜

厚度损失为0%。用实施例1的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约40 nm厚的薄膜，并在200℃下烘烤60秒。然后涂布500 nm厚的实施例1的光刻胶溶液并在115℃下烘烤60秒。然后将该基片用193 nm的曝光工具进行成像曝光。将已曝光的基片在110℃下烘烤60秒并用氢氧化四甲基铵的2.38 wt%水溶液显影60秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例5

通过将3 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚物、0.9 g 2,6-双羟甲基对甲酚和0.0039 g甲苯磺酸对硝基苄基酯溶于27 g乳酸乙酯中，制备防反射涂料组合物。将该溶液通过0.45和0.2 μm过滤器过滤。按实施例2所述获得该防反射涂料的n（折射率）和k（吸收参数）。测得折射率为1.466，吸收参数为0.576。在200℃下烘烤60秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡60秒后测得薄膜厚度损失为0%。用实施例1的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约40 nm厚的薄膜，并在200℃下烘烤60秒。然后涂布500 nm厚的实施例1的光刻胶溶液并在115℃下烘烤60秒。然后将该基片用193 nm的曝光工具进行成像曝光。将已曝光的基片在110℃下烘烤60秒并用氢氧化四甲基铵的2.38 wt%水溶液显影60秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例6

通过将3 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚物、0.9 g Cymel® 324（购自Cytec Industries, West Paterson, New Jersey）和0.0195 g甲苯磺酸对硝基苄基酯溶于27 g乳酸乙酯中，制备防反射涂料组合物。将该溶液通过0.45和0.2 μm过滤器过滤。按实施例2所述获得该防反射涂料的n（折射率）和k（吸收参数）。

测得折射率为1.466，吸收参数为0.576。在200℃下烘烤60秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡60秒后测得薄膜厚度损失为0%。用实施例1的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约40 nm厚的薄膜，并在200℃下烘烤60秒。然后涂布500 nm厚的实施例1的光刻胶溶液并在115℃下烘烤60秒。然后将该基片用193 nm的曝光工具进行成像曝光。将已曝光的基片在110℃下烘烤60秒并用氢氧化四甲基铵的2.38 wt%水溶液显影60秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例7

通过将0.75 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚物、0.112 g Cymel® 324（购自Cytec Industries，West Paterson，New Jersey）、0.1 12 g 2,6-双(羟甲基对甲酚)和0.0097 g甲苯磺酸对硝基苄基酯溶于36.25 g乳酸乙酯中，制备防反射涂料组合物。将该溶液通过0.45和0.2 μm过滤器过滤。按实施例2所述获得该防反射涂料的n（折射率）和k（吸收参数）。测得折射率为1.452，吸收参数为0.555。在200℃下烘烤60秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡60秒后测得薄膜厚度损失为0%。用实施例1的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约40 nm厚的薄膜，并在200℃下烘烤60秒。然后涂布500 nm厚的实施例1的光刻胶溶液并在115℃下烘烤60秒。然后将该基片用193 nm的曝光工具进行成像曝光。将已曝光的基片在110℃下烘烤60秒并用氢氧化四甲基铵的2.38 wt%水溶液显影60秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例8

通过将0.75 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚

物、0.224 g 四(甲氧基甲基)甘脲（Powderlink®，购自 Cytec Industries，West Paterson，New Jersey）和 0.0097 g 甲苯磺酸对硝基苄基酯溶于 36.25 g 乳酸乙酯中，制备防反射涂料组合物。将该溶液通过 0.45 和 0.2 μm 过滤器过滤。按实施例 2 所述获得该防反射涂料的 n（折射率）和 k（吸收参数）。测得折射率为 1.442，吸收参数为 0.532。在 200℃ 下烘烤 60 秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡 60 秒后测得薄膜厚度损失为 0%。用实施例 1 的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约 40 nm 厚的薄膜，并在 200℃ 下烘烤 60 秒。然后涂布 500 nm 厚的实施例 1 的光刻胶溶液并在 115℃ 下烘烤 60 秒。然后将该基片用 193 nm 的曝光工具进行成像曝光。将已曝光的基片在 110℃ 下烘烤 60 秒并用氢氧化四甲基铵的 2.38 wt% 水溶液显影 60 秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例 9

通过将 0.75 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚物、0.13 g 六甲氧基甲基三聚氰胺和 0.0097 g 甲苯磺酸对硝基苄基酯溶于 36.25 g 乳酸乙酯中，制备防反射涂料组合物。将该溶液通过 0.45 和 0.2 μm 过滤器过滤。按实施例 2 所述获得该防反射涂料的 n（折射率）和 k（吸收参数）。测得折射率为 1.445，吸收参数为 0.545。在 200℃ 下烘烤 60 秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡 60 秒后测得薄膜厚度损失为 0%。用实施例 1 的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约 40 nm 厚的薄膜，并在 200℃ 下烘烤 60 秒。然后涂布 500 nm 厚的实施例 1 的光刻胶溶液并在 115℃ 下烘烤 60 秒。然后将该基片用 193 nm 的曝光工具进行成像曝光。将已曝光的基片在 110℃ 下烘烤 60 秒并用氢氧化四甲基铵的 2.38 wt% 水溶液显影 60 秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例 10

通过将 0.75 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚物、0.224 g 六甲氧基甲基三聚氰胺和 0.0195 g 甲苯磺酸对硝基苄基酯溶于 36.25 g 乳酸乙酯中，制备防反射涂料组合物。将该溶液通过 0.45 和 0.2 μm 过滤器过滤。按实施例 2 所述获得该防反射涂料的 n（折射率）和 k（吸收参数）。测得折射率为 1.455，吸收参数为 0.536。在 200℃下烘烤 60 秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡 60 秒后测得薄膜厚度损失为 0%。用实施例 1 的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约 40 nm 厚的薄膜，并在 200℃下烘烤 60 秒。然后涂布 500 nm 厚的实施例 1 的光刻胶溶液并在 115℃下烘烤 60 秒。然后将该基片用 193 nm 的曝光工具进行成像曝光。将已曝光的基片在 110℃下烘烤 60 秒并用氢氧化四甲基铵的 2.38 wt% 水溶液显影 60 秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例 11

通过将 0.75 g 4-羟基苯乙烯与甲基丙烯酸甲酯(52:48)的共聚物、0.32 g 四（甲氧基甲基）甘脲（Powderlink®，购自 Cytec Industries, West Paterson, New Jersey）和 0.0214 g 甲苯磺酸对硝基苄基酯溶于 36.40 g 乳酸乙酯中，制备防反射涂料组合物。将该溶液通过 0.45 和 0.2 μm 过滤器过滤。按实施例 2 所述获得该防反射涂料的 n（折射率）和 k（吸收参数）。测得折射率为 1.456，吸收参数为 0.542。在 200℃下烘烤 60 秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡 60 秒后测得薄膜厚度损失为 0%。用实施例 1 的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约 40 nm 厚的薄膜，并在 200℃下烘烤 60 秒。然后涂布 500 nm 厚的实施例 1 的光刻胶溶液并在 115℃下烘烤 60 秒。然后将该基片用 193 nm 的曝光工具进行成像曝光。将已曝光的基片在 110℃下烘烤 60 秒并用氢氧化四甲基铵的 2.38 wt% 水溶液显影 60 秒。在扫描电子显微镜

下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例 12

将 35.6 g (0.2 mol) 甲基丙烯酸 2-羟苯基酯、5.01 (0.05 mol) g 甲基丙烯酸甲酯溶于 60.92 g 无水四氢呋喃中，向该溶液中加入 4.06 g 2,2′-偶氮二异丁腈(AIBN)。将该物料在 70℃下在氮气气氛下搅拌 5 小时。将该粘性溶液倒入异丙醇中，洗涤该沉淀物，并在异丙醇中再沉淀两次。如此分离出 40 g 聚合物，将其真空干燥。

实施例 13

通过将 1.0 g 实施例 12 中制备的甲基丙烯酸 2-羟苯基酯与甲基丙烯酸甲酯的共聚物、0.32 g 四(甲氧基甲基)甘脲（Powderlink®，购自 Cytec Industries，West Paterson，New Jersey）和 0.013 g 甲苯磺酸对硝基苄基酯溶于 49.0 g 乳酸乙酯中，制备防反射涂料组合物。将该溶液通过 0.45 和 0.2 μm 过滤器过滤。按实施例 2 所述获得该防反射涂料的 n（折射率）和 k（吸收参数）。测得折射率为 1.806，吸收参数为 0.58。在 200℃下烘烤 60 秒并在丙二醇单甲醚乙酸酯(PGMEA)中浸泡 60 秒后测得薄膜厚度损失为 0%。用实施例 1 的光刻胶评估该防反射涂料配方的性能。在硅片上用本实施例的防反射涂料配方涂布约 40 nm 厚的薄膜，并在 200℃下烘烤 60 秒。然后涂布 500 nm 厚的实施例 1 的光刻胶溶液并在 115℃下烘烤 60 秒。然后将该基片用 193 nm 的曝光工具进行成像曝光。将已曝光的基片在 110℃下烘烤 60 秒并用氢氧化四甲基铵的 2.38 wt% 水溶液显影 60 秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。

实施例 14

将 53.4 g (0.3 mol) 甲基丙烯酸邻羟基苯基酯溶于 80.1 g 无水四氢呋喃中，向该溶液中加入 5.34 g 2,2′-偶氮二异丁腈(AIBN)。

将该物料在70℃下在氮气气氛下搅拌5小时。将该粘性溶液倒入异丙醇中，洗涤该沉淀物，并在异丙醇中再沉淀两次。如此分离出40 g聚合物，将其真空干燥。

实施例15

通过将1.0 g实施例14中制备的聚(甲基丙烯酸2-羟基苯基酯)、0.294 g四(甲氧基甲基)甘脲(Powderlink®，购自Cytec Industries，West Paterson，New Jersey)和0.013 g甲苯磺酸对硝基苄基酯溶于49 g乳酸乙酯中，制备防反射涂料组合物。将该溶液通过0.45和0.2 μm过滤器过滤。通过将涂有该防反射组合物的硅片在220℃温度下烘烤60秒，然后用椭圆测量仪在193 nm处测量n和k值，获得n值(折射率)和k值(吸收参数)。测得折射率为1.8087，吸收参数为0.652。在硅片上用本实施例的防反射涂料配方涂布约40 nm厚的薄膜。然后涂布500 nm厚的实施例1的光刻胶溶液并在115℃下烘烤60秒。然后将该基片用193 nm的曝光工具进行成像曝光。将已曝光的基片在110℃下烘烤60秒并用氢氧化四甲基铵的2.38 wt%水溶液显影60秒。在扫描电子显微镜下观察，线路和间隔图形显示无驻波，说明该底部防反射涂层有效。