



159159

TITLE

Copolymer for gap filling material composition, preparation method thereof and gap filling material composition for antireflective coating layer

5 BACKGROUND

1. Field of the Invention

The present invention relates to a copolymer for a gap filling material functioning as an antireflective coating layer, a method of manufacturing a copolymer for gap filling material, and a gap filling material composition including a copolymer
10 for a gap filling material.

2. Description of the Related Art

Recently, as a semiconductor device is high-integrated, a hyperfine pattern less than or equal to 0.10 microns has been required for manufacturing in Ultra-Large Scale
15 Integration (ULSI), and the like. Also, a lithography process using a wavelength much shorter than a wavelength of a conventional g-ray and i-ray area has been used. That is, a dual damascene is a method of forming fine wiring, and is a mainstream method used in a manufacturing process for a fine semiconductor integrated circuit device. A damascene process forms a fine wiring groove on an insulating layer of a semiconductor
20 substrate, accumulates a metal-layer on the insulating layer including an inside of the wiring groove, and eliminates metal-layer outside the wiring groove by using a chemical mechanical polishing (CMP) scheme, thereby generating a fine buried wiring inside the wiring groove. Also, the damascene process may be classified into a single



damascene and the dual damascene.

The dual damascene process forms a via hole for accessing a bottom-layered wiring, at a lower part of a wiring groove formed on an insulating layer, and buries a metal-layer to both the wiring groove and the via hole at the same time to form a wire, thereby reducing a number of processes to be progressing. The single damascene process forms a metal-plug inside a via hole in advance and forms a buried wire inside the wiring groove.

According to the dual damascene process, a semiconductor device is formed on a semiconductor substrate, and a bottom-layered wiring is formed on an upper part of the semiconductor device. The insulating layer is accumulated on a top of the bottom-layered wiring, an antireflective coating layer is formed on the insulating layer, and a photoresist layer is formed on the antireflective coating layer. The photoresist layer is exposed to light by using a photomask where a via hole pattern is formed, and is continuously developed, and thus, a pattern where an area of the via hole is opened is transcribed to the photoresist layer. The antireflective coating layer is formed for preventing lowering of a resolution and transmitting, to the photoresist layer, a light reflected by a surface of the bottom-layered wiring, when the photoresist layer is exposed to light. An antireflective coating layer formed on a bottom layer of the photoresist layer is referred to as a bottom anti reflective coating (BARC). Dry etching is performed with respect to the antireflective coating layer and insulating layer, to form the via hole on the insulating layer by using the photoresist layer as a mask. The photoresist layer and the antireflective coating layer are eliminated and an inside of the via hole is filled with a gap filling material. The gap filling material includes a dielectric composition nearly identical to a composition of the antireflective coating

layer. To fill the inside of the via hole with the gap filling material, the gap filling material is accumulated on the insulating layer including the inside of the via hole, and the gap filling material on the outside the via hole is eliminated through an etchback process. When the etch back process is performed, a surface of the gap filling material filling the via hole becomes even, and a height of the surface is nearly the same as a surface of the insulating layer. A second antireflective coating layer is formed on the insulating layer, and a second photoresist layer is formed on the second antireflective coating layer. The second photoresist layer is exposed to light by using a photomask where a wiring groove pattern is formed, and is continuously developed, and thus, a pattern where an area of the via hole is opened is transcribed to the second photoresist layer. Dry etching is performed with respect to the second antireflective coating layer and is continuously performed to a middle of the inter-layer dielectric, thereby forming a wiring groove on a top of the via hole. The second antireflective layer is eliminated after the second photoresist layer is eliminated. When the second antireflective layer is eliminated, the gap filling material filling the via hole is also eliminated, and the surface of the bottom-layered wiring is exposed at a lower part of the via hole. A copper wiring is formed inside the via hole and wiring groove. A copper-layer is formed, by a sputtering scheme or a gold-plating scheme, on the insulating layer including an inside of the via hole and the wiring groove, and the copper-layer outside the wiring groove is eliminated by the CMP scheme.

The gap filling material that is used in the damascene process does not have an anti-reflecting function, and only has a gap-filling function when the via hole and a trench are pattern-processed on the semiconductor substrate. Conventionally, a material having a high optical density has been used for burying the via hole and a

contact hole in the dual damascene process. However, occasionally, the gap filling material is insufficiently filled or a void is generated although the gap filling material fills the via hole and contact hole. Also, when a composition of the gap filling material is not light-absorptive, the antireflective coating layer needs to be separately
 5 inserted during a trench patterning process or the antireflective coating layer is required to be coated over the composition of the gap filling material before performing coating of the photoresist, thereby having an unnecessarily high unit cost of manufacturing. To date, a material that has the anti-reflecting function and evenly fills the via hole has been insufficiently developed.

10

SUMMARY

An aspect of the present invention provides a gap filling material composition that fills an uneven substrate without a void and improves evenness, thereby increasing a process margin when a lithograph process of a photoresist is performed.

15

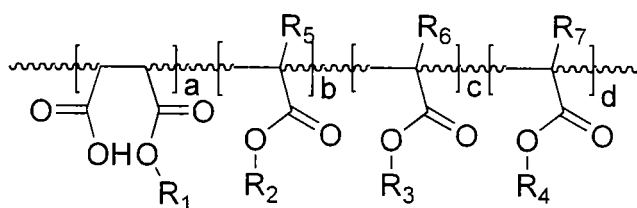
Another aspect of the present invention also provides a copolymer for a gap filling material included in a gap filling material composition, and a preparation method thereof.

According to an aspect of the present invention, there is provided a copolymer for a gap filling material functioning as an antireflective coating layer, as expressed in

20

Chemical Formula 1 below,

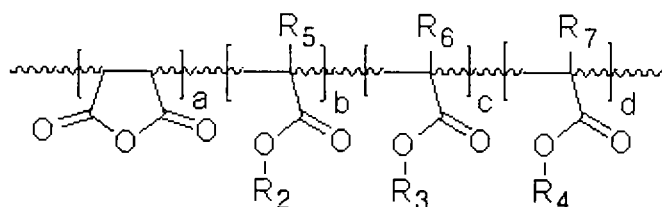
[Chemical Formula 1]



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are independent from each other, R_1 is hydrogen or a C1-10 alkyl group, each of R_2 , R_3 , and R_4 indicates hydrogen, the C1-10 alkyl group, or a C1-20 arylalkyl group, each of R_5 , R_6 , and R_7 indicates hydrogen or a methyl group, and each of a, b, c, and d is a number indicating a repeating unit in a main chain, where $a+b+c+d = 1$, $0.05 < a/(a+b+c+d) < 0.95$, $0.05 < b/(a+b+c+d) < 0.95$, $0.05 < c/(a+b+c+d) < 0.95$, and $0.05 < d/(a+b+c+d) < 0.95$.

According to an aspect of the present invention, there is provided a method of manufacturing the copolymer for a gap filling material of Chemical Formula 1, the method including performing polymerization of a maleic acid anhydride and an acrylate compound to generate a polymer as expressed in Chemical Formula 2 below; and performing reaction of the polymer of Chemical Formula 2 with the a copolymer and C1-10 alkyl alcohol,

[Chemical Formula 2]



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are independent from each other, R_1 is hydrogen or a C1-10 alkyl group, each of R_2 , R_3 , and R_4 indicates hydrogen, the C1-10 alkyl group, or a C1-20 arylalkyl group, each of R_5 , R_6 , and R_7 indicates hydrogen or a methyl group, and each of a, b, c, and d is a number indicating a repeating unit in a main chain, where $a+b+c+d = 1$, $0.05 < a/(a+b+c+d) < 0.95$, $0.05 < b/(a+b+c+d) < 0.95$, $0.05 < c/(a+b+c+d) < 0.95$, and $0.05 < d/(a+b+c+d) < 0.95$.

The polymerization is at least one of a bulk polymerization, a solution

polymerization, a suspension polymerization, a bulk-suspension polymerization, an emulsion polymerization, and a radical polymerization.

The gap filling material composition is spread on a top of a layer to be etched, the spread composition is hardened through a baking process, and the gap filling material is accumulated. Also, a photoresist is formed on a top of the gap filling material, the formed photoresist is exposed and developed to form a photoresist pattern, the gap filling material is etched by using the photoresist pattern as an etching mask, and the layer is etched to form a pattern of the layer.

Additional aspects, features, and/or advantages of the invention will be set forth in part in the description which follows and, in part, will be apparent from the description, or may be learned by practice of the invention.

BRIEF DESCRIPTION OF THE DRAWINGS

These and/or other aspects, features, and advantages of the invention will become apparent and more readily appreciated from the following description of exemplary embodiments, taken in conjunction with the accompanying drawings of which:

FIG. 1 is a scanning electron microscope image of a gap filling material composition of Example 1 which is spread on a substrate.

DETAILED DESCRIPTION

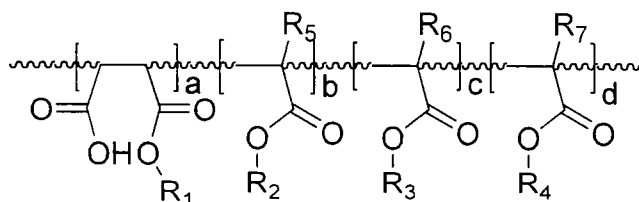
Reference will now be made in detail to exemplary embodiments of the present invention, examples of which are illustrated in the accompanying drawings,

wherein like reference numerals refer to the like elements throughout. Exemplary embodiments are described below to explain the present invention by referring to the figures.

Hereinafter, a copolymer for a gap filling material functioning as an
 5 antireflective coating layer is described.

The copolymer for the gap filling material having a function of the antireflective coating layer is expressed in Chemical Formula 1 below.

[Chemical Formula 1]



10 Here, R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are independent from each other, R_1 is hydrogen or a C1-10 alkyl group, each of R_2 , R_3 , and R_4 indicates hydrogen, the C1-10 alkyl group, or a C1-20 arylalkyl group, and each of R_5 , R_6 and R_7 indicates hydrogen or a methyl group. Also, each of a, b, c, and d is a number indicating a repeating unit in a main chain, where $a+b+c+d = 1$, $0.05 < a/(a+b+c+d) < 0.95$, $0.05 < b/(a+b+c+d) < 0.95$,
 15 $0.05 < c/(a+b+c+d) < 0.95$, and $0.05 < d/(a+b+c+d) < 0.95$.

A structure of the gap filling material may be variously designed. A first is adjusting an average molecular weight to be low to increase filling ability, a second is providing a light-absorptive material of light-absorptive chemicals to a main chain of a polymer, and a third is respectively using the light-absorptive material and a hardening
 20 agent polymer that is not able to absorb light. In general, the light-absorptive material is separately used for adjusting an amount of the light-absorptive chemicals. Also, a hydroxyl functional group, a glycidyl functional group, or an acetyl functional group is

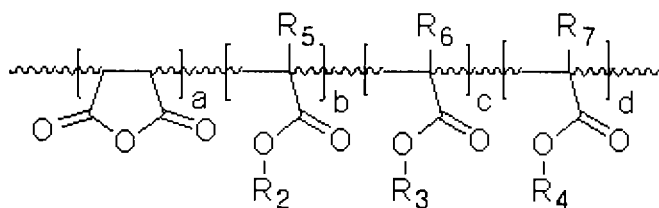
mainly used as the hardening agent polymer.

The copolymer for the gap filling material functioning as the antireflective coating layer expressed in the above Chemical Formula 1 introduces a carboxyl group to enable light-absorption and thermosetting, and includes a maleic acid anhydride known as having an excellent etching speed.

Hereinafter, a method of manufacturing the copolymer for the gap filling material functioning as the antireflective coating layer according to an embodiment will be described in detail.

The copolymer for the gap filling material functioning as the antireflective coating layer expressed in Chemical Formula 1 is manufactured through manufacturing a polymer of Chemical Formula 2 by performing polymerization of the maleic acid anhydride and an acrylate compound, and performing a reaction of a reaction intermediate of Chemical Formula 2 and alkyl alcohol.

[Chemical Formula 2]



Here, R₂, R₃, R₄, R₅, R₆, and R₇ are independent from each other, each of R₂, R₃, and R₄ indicates hydrogen, the C1-10 alkyl group, or a C1-20 arylalkyl group, each of R₅, R₆, and R₇ indicates hydrogen or a methyl group, and each of a, b, c, and d is a number indicating a repeating unit in a main chain, where $a+b+c+d = 1$, $0.05 < a/(a+b+c+d) < 0.95$, $0.05 < b/(a+b+c+d) < 0.95$, $0.05 < c/(a+b+c+d) < 0.95$, and $0.05 < d/(a+b+c+d) < 0.95$.

In this instance, the acrylate compound is at least one selected from a group consisting of methyl acrylate, ethyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate, isobornyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-propyl methacrylate, tert-butyl methacrylate, n-
5 butyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, diethylene glycol monomethyl ether methacrylate, 2-ethylhexyl methacrylate, benzyl methacrylate, 1-naphthylmethyl methacrylate, 2-naphthylmethyl methacrylate, 9-anthrylmethyl methacrylate, 1-anthrylmethyl methacrylate, and 2-anthrylmethyl methacrylate.

10 A carboxyl group reacts with the hardening agent having a functional group such as acetal and the like to form a crosslinking structure, the carboxyl group being manufactured by ring-opening of the reaction intermediate of Chemical Formula 2 with alkyl alcohol. The gap filling material using the copolymer manufactured according to an embodiment is spread on a substrate and is hardened during a baking process, thereby
15 having a dissolution resistance against a solvent. That is, the gap filling material fills a contact hole and a via hole, and becomes insoluble in a photoresist solvent after the photoresist is spread, thereby having a stability. Accordingly, the copolymer manufactured according to an embodiment of the present invention may be used as the hardening agent polymer in the gap filling material composition.

20 When the polymer of Chemical Formula 2 is manufactured, a regular polymerization, such as a bulk polymerization, a solution polymerization, a suspension polymerization, a bulk-suspension polymerization, an emulsion polymerization, and the like, may be used, and a radical polymerization is preferable. A general radical polymerization initiator, such as azobisisobutyronitrile, benzoyl peroxide, lauryl

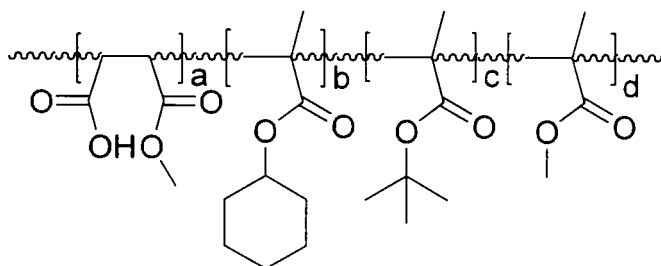
peroxide, azobisisobutyronitrile, azobisisobutyronitrile, and t-butyl hydroperoxide, and the like, is used without limit, as an initiator for the radical polymerization.

A polymerization solvent is at least one selected from benzene, toluene, xylene, halogenated benzene, diethyl ether, tetrahydrofuran, esters, ethers, lactones, ketones, and amides. A polymerization temperature is appropriately selected depending on a type of the initiator. A molecular weight distribution of the polymer is appropriately adjusted by changing an amount of the polymerization initiator and a reaction time. After the polymerization is finished, by-products and an unreacted monomer remaining in a reaction compound need to be eliminated by an extraction or a precipitation using a solvent. When a ring-opened maleic acid anhydride is included in the reaction compound, there is a difficulty in obtaining a desired molecular weight through a regular gel permeation chromatography due to generated carboxylic acid. Accordingly, a molecular weight of the polymer of Chemical Formula 2 which is a polymer prior to being ring-opened with C1-10 alcohol is referenced when the molecular weight is adjusted. That is, a weight-averaged molecular weight of the polymer of Chemical Formula 2 in terms of polystyrene through the gel permeation chromatography is about 1,000 to about 100,000. Here, the polymer of Chemical Formula 2 is the polymer before being ring-opened. Also, the weight-averaged molecular weight of the polymer of Chemical Formula 2 is preferably about 5,000 to about 10,000 considering a solubility of the solvent, a spreading characteristic, and a sufficient crosslinking. Also, the molecular weight distribution of the polymer (PDI) is preferably about 1.0 to about 5.0, and particularly preferably about 1.5 to about 3.5.

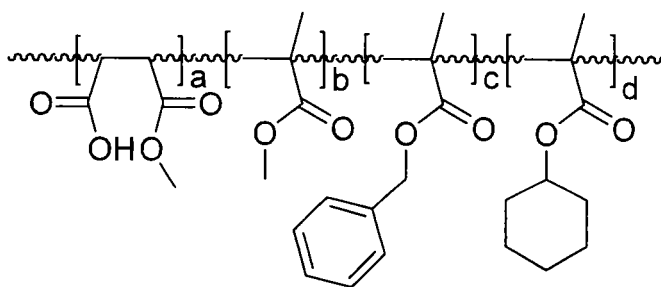
Polymers expressed in Chemical Formulas 3 to 6 are detailed examples of the polymer expressed in Chemical Formula 1. However, the examples are not limited

thereto.

[Chemical Formula 3]

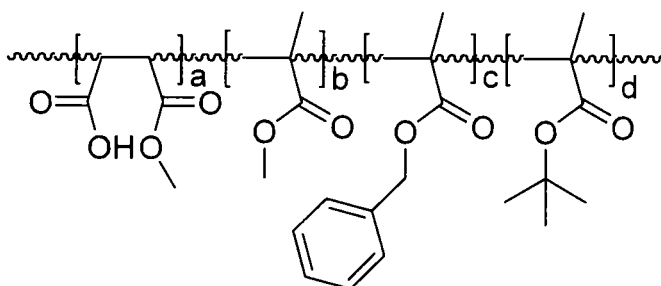


[Chemical Formula 4]

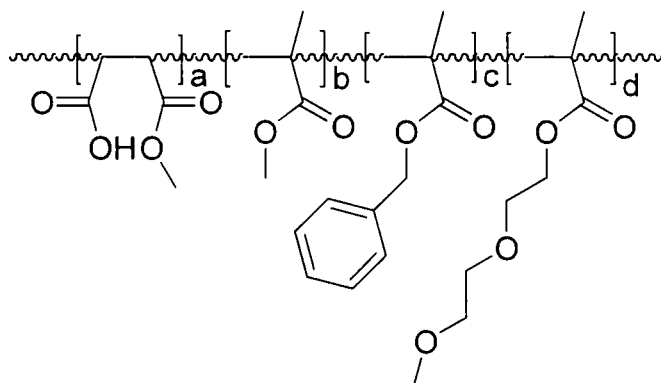


5

[Chemical Formula 5]



[Chemical Formula 6]

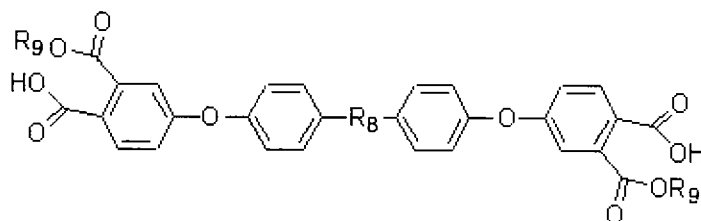


Here, each of a, b, c, and d is a number indicating a repeating unit in a main chain, where $a+b+c+d=1$, $0.05 < a/(a+b+c+d) < 0.95$, $0.05 < b/(a+b+c+d) < 0.95$, $0.05 < c/(a+b+c+d) < 0.95$, and $0.05 < d/(a+b+c+d) < 0.95$.

5 Hereinafter, a gap filling material composition for antireflective coating layer according to an embodiment of the present invention will be described in detail.

The gap filling material composition according to an embodiment of the present invention may include an additive to improve performance and hardening of the polymer and a light-absorptive material in addition to the copolymer for the gap filling material of Chemical Formula 1, and the additive may include a crosslinking agent and a thermal acid generator. The gap filling material composition according to an embodiment of the present invention may include a compound including a light-absorptive light or may include a light-absorptive material separate from a polymer that is not light-absorptive. In general, the light-absorptive material is separately used to control an amount of light-absorptive chemicals. The light-absorptive material is a polymer including a crosslinking site at an end of a side-chain or a straight-chain, and also includes a monomer-typed light-absorptive material expressed in Chemical Formulas 7 and 8.

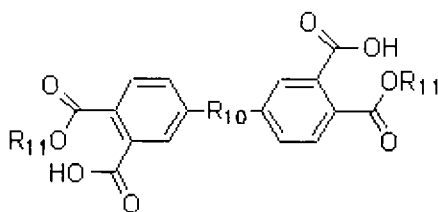
[Chemical Formula 7]



Here, R₈ is —O— , $\text{—S(=O)}_2\text{—}$, $\text{—C(CH}_3)_2\text{—}$ or —C(=O)— , and R₉ independently

indicates hydrogen, a C1-10 alkyl, or a C1-10 alkoxy.

[Chemical Formula 8]



Here, R₁₀ is —O— , $\text{—S(=O)}_2\text{—}$, $\text{—C(CH}_3)_2\text{—}$ or —C(=O)— , and R₁₁

independently indicates hydrogen, a C1-10 alkyl, or a C1-10 alkoxy.

The crosslinking agent is a compound containing at least two crosslinking functional groups, and examples of the crosslinking agent include an aminoplastic compound, a multi-functional epoxy resin, and a mixture of dianhydride. Also, the crosslinking agent is at least one selected from a group consisting of oxetanyl, oxazolin, cyclocarbonate, alcohol silyl, aminomethylol, alkoxymethyl, aziridinyl, methylol, isocyanate, alkoxymethylamino, and multifunctional epoxy.

Examples of the aminoplastic compound include dimethoxymethylglycouril, diethoxymethylglycouril, a mixture of dimethoxymethylglycouril and

diethoxymethylglycouril, diethyldimethylmethylglycouril, tetramethoxymethylglycouril, hexamethoxymethyl melamine resin, and the like. Also, MY720, CY179MA, DENACOL, and the like may be used as the multifunctional epoxy.

It is preferable to use the thermal acid generator as a catalyst to accelerate a
5 hardening reaction. As an example, the thermal acid generator is at least one selected from a group consisting of toluenesulfonic acid, amine salt of toluenesulfonic acid, pyridine salt of toluenesulfonic acid, alkylsulfonic acid, amine salt of alkylsulfonic acid, and pyridine salt of alkylsulfonic acid.

An organic solvent used for the gap filling material composition is at least one
10 selected from a group consisting of propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), cyclohexanone, ethyl lactate, propylene glycol n-propyl ether, dimethylformamide (DMF), γ -butyrolactone, ethoxy ethanol, methoxy ethanol, methyl 3-methoxy propionate (MMP), and ethyl 3-ethoxypropionate (EEP).

15 The gap filling material composition according to an embodiment or the present invention includes about 0.1 w% to about 40 w% of light-absorptive material in a total composition, and preferably includes about 0.01 w% to about 15 w% of light-absorptive material in the total composition. Also, the gap filling material composition preferably includes about 0.1 w% to about 20 w% of polymer in the total composition, includes
20 about 0.01 w% to about 15 w% of the crosslinking agent in the total composition, and includes about 0.01 w% to about 20 w% and more preferably about 0.01 w% to about 15 w% of the thermal generator in the total composition.

According to an embodiment of the present invention, when a thermal process, such as baking and the like, is performed after the gap filling material composition is

spread on a wafer, acid is generated from the thermal acid generator, a crosslinking reaction between the light-absorptive material, the polymer, and the crosslinking agent that is used as the additive is accelerated with the generated thermal acid, and thus, a gap filling material that is insoluble in an organic solvent is generated. The gap filling material fills the via hole and the contact hole, and thereby the fine wiring is formed through the dual damascene process.

Hereinafter, a method of forming a pattern of a semiconductor device using the gap filling material composition according to an embodiment of the present invention will be described in detail. The method includes spreading an organic gap filling material composition on a top of a layer to be etched, hardening the spread composition through a baking process, forming a crosslink to form accumulation of the gap filling material, spreading a photoresist on a top of the gap filling material, exposing and developing to form a photoresist pattern, etching the gap filling material by using the photoresist pattern as an etching mask, and etching the layer to form a pattern of the layer.

The baking process is preferably performed at a temperature of about 150 °C to about 250 °C for about 30 seconds to about 5 minutes. Also, after a hard mask is spread, the baking process may be additionally performed before or after laminating an organic/inorganic gap filling material composition on a top of a generated spin-on carbon hard mask, and the baking process is preferably performed at a temperature of about 70 °C to 200 °C.

Hereinafter, examples will be described in detail.

[Synthesis Examples]

Synthesis Example 1: synthesis of polymer A for gap filling material

20g maleic acid anhydride, 20.42g methyl methacrylate, 34.31g cyclohexyl metacrylate, 29g tert-butyl methacrylate, and 10.37g AIBN was dissolved in 342g 1,4-dioxane and a polymerization reaction was performed at a temperature of about 80 °C for four hours. After the polymerization reaction was finished, the reaction solution was dropped to methyl alcohol to filter out a generated precipitate, and was vacuum-dried after being washed with methyl alcohol several times (molecular weight: 7800, PDI: 2.84, yield: 60%). 62.23g vacuum dried polymer and 1.03g and toluenesulfonic acid monohydrate was mixed with 342g methyl alcohol, and a reaction was performed at a temperature of about 80 °C for 20 hours. After the reaction was finished, the reaction solution was dropped to distilled water to filter out a generated precipitate, and was vacuum-dried after being washed with distilled water (yield: 58%).

Synthesis Example 2: synthesis of polymer B for gap filling material

20g maleic acid anhydride, 20.42g methyl methacrylate, 34.31g cyclohexyl metacrylate, 35.93g benzyl methacrylate, and 11.06g AIBN was dissolved in 365g 1,4-dioxane and a polymerization reaction was performed at a temperature of about 80 °C for four hours. After the polymerization reaction was finished, the reaction solution was dropped to methyl alcohol to filter out a generated precipitate, and was vacuum-dried after being washed with methyl alcohol several times (molecular weight: 7800, PDI: 2.79, yield: 59%). 65.28g vacuum dried polymer and 1.1g toluenesulfonic acid monohydrate was mixed with 365g methyl alcohol, and reaction was performed at a temperature of about 80 °C for 20 hours. After the reaction was finished, the reaction solution was dropped to distilled water to filter out a generated precipitate, and was vacuum-dried after being washed with distilled water (yield: 59%).

Synthesis Example 3: synthesis of polymer C for gap filling material

20g maleic acid anhydride, 20.42g methyl methacrylate, 35.93g benzyl methacrylate, 29g tert-butyl methacrylate, and 10.53g AIBN was dissolved in 347g 1,4-dioxane and a polymerization reaction was performed at a temperature of about 80 °C for four hours. After the polymerization reaction was finished, the reaction solution was dropped to methyl alcohol to filter out a generated precipitate, and was vacuum-dried after being washed with methyl alcohol several times (molecular weight: 7800, PDI: 2.82, yield: 58%). 60.1g vacuum dried polymer and 1g toluenesulfonic acid monohydrate was mixed with 347g methyl alcohol, and reaction was performed at a temperature of about 80 °C for 20 hours. After the reaction was finished, the reaction solution was dropped to distilled water to filter out a generated precipitate, and was vacuum-dried after being washed with distilled water (yield: 59%).

Synthesis Example 4: synthesis of polymer D for gap filling material

20g maleic acid anhydride, 20.42g methyl methacrylate, 35.93g benzyl methacrylate, 38.38g diethylene glycol methylether methacrylate, and 11.47g AIBN was dissolved in 378g 1,4-dioxane and a polymerization reaction was performed at a temperature of about 80 °C for four hours. After the polymerization reaction was finished, the reaction solution was dropped to methyl alcohol to filter out a generated precipitate, and was vacuum-dried after being washed with methyl alcohol several times (molecular weight: 7800, PDI: 2.94, yield: 62%). 71.1g vacuum dried polymer and 1.1g toluenesulfonic acid monohydrate was mixed with 378g methyl alcohol, and a reaction was performed at a temperature of about 80 °C for 20 hours. After the reaction was finished, the reaction solution was dropped to distilled water to filter out a generated precipitate, and was vacuum-dried after being washed with distilled water (yield: 60%).

[Examples]

Example 1: manufacturing of gap filling material composition A

1.90g polymer for a gap filling material manufactured by Synthesis Example 1, 2.85g light-absorptive material, 1.43g tetramethoxymethylglycouril, and 0.10g thermal
5 generator was dissolved in 93.73g propylene glycol monomethyl ether acetate (PGMEA), and the solution was filtered through a membrane filter having a diameter of 0.2 μm , and thus, the gap filling material composition A was manufactured.

Example 2: manufacturing of gap filling material composition B

1.90g polymer for a gap filling material manufactured by Synthesis Example 2,
10 2.85g light-absorptive material, 1.43g tetramethoxymethylglycouril, and 0.10g thermal generator was dissolved in 93.73g PGMEA, and the solution was filtered through a membrane filter having a diameter of 0.2 μm , and thus, the gap filling material composition B was manufactured.

Example 3: manufacturing of gap filling material composition C

15 1.90g polymer for a gap filling material manufactured by Synthesis Example 3, 2.85g light-absorptive material, 1.43g tetramethoxymethylglycouril, and 0.10g thermal generator was dissolved in 93.73g PGMEA, and the solution was filtered through a membrane filter having a diameter of 0.2 μm , and thus, the gap filling material composition C was manufactured.

20 Example 4: manufacturing of gap filling material composition D

1.90g polymer for a gap filling material manufactured by Synthesis Example 4, 2.85g light-absorptive material, 1.43g tetramethoxymethylglycouril, and 0.10g thermal generator was dissolved in 93.73g PGMEA, and the solution was filtered through a membrane filter having a diameter of 0.2 μm , and thus, the gap filling material

composition D was manufactured.

[Test Examples]

Test Example 1: stripping test

A gap filling material composition was spin-spread on a silicon wafer, and
5 baked for one minute on a plate heated to about 230 °C, and thereby a layer for gap
filling material is formed. In this instance, the gap filling material may be
manufactured by Examples 1 through 4. After crosslinking, a thickness of the layer
for the gap filling material was measured, and the wafer coated with the layer for the
gap filling material was dip in a solvent, ethyl lactate, for one minute. After
10 completely eliminating ethyl lactate, the wafer was baked for one minute on a plate
heated to about 100 °C, and the thickness of the layer for the gap filling material was
measured again. As a result of the measurement, there was no difference in the
thickness of the layer for the layer between before processing ethyl lactate and after
processing ethyl lactate, with respect to all gap filling material compositions
15 manufactured by Examples 1 through 4. Accordingly, since the gap filling material
compositions manufactured by the examples is completely hardened, the gap filling
material compositions was not intermixed with the photoresist while a lithography
process is performed.

Test Example 2: checking filling-characteristic of layer for gap filling material

20 A gap filling material compositions filled a contact hole and a via hole of a dual
damascene process and was spin coated on a substrate, and was baked for one minute on
a plate heated to about 230 °C, and thereby the layer for the gap filling material was
manufactured. In this instance, the gap filling material may be manufactured by
Examples 1 through 4. The layer for the gap filling material was identified through a

scanning electron microscope.

FIG. 1 is a scanning electron microscope image of the gap filling material composition of Example 1 which is spread on a substrate. Referring to FIG. 1, a void does not occur during a filling process of the dual damascene process. Also, the gap
5 filling material composition has over 95% of a sufficient filling-characteristic and has an excellent surface evenness after filling.

Although a few exemplary embodiments of the present invention have been shown and described, the present invention is not limited to the described exemplary embodiments. Instead, it would be appreciated by those skilled in the art that changes
10 may be made to these exemplary embodiments without departing from the principles and spirit of the invention, the scope of which is defined by the claims and their equivalents.

According to the embodiments, a gap filling material composition that is not intermixed with a photoresist, has an excellent filling characteristic, has an excellent
15 adhesive property and safekeeping property, and has a fast dry etching speed, may be obtained.

According to the embodiments, a void does not occur during a filling process of a dual damascene process, and a gap filling material composition sufficiently is filled so as to have over 95% of evenness.

20 Also, according to the embodiments, a gap filling material composition is able to sufficiently absorb reflective light occurring when the gap filling material composition is exposed to light during a lithography process after being filled.

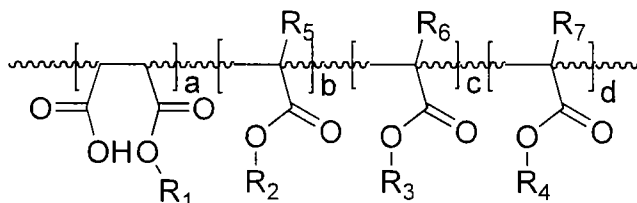
Also, the gap filling material composition is not intermixed with a photoresist, an antireflective coating layer, a dielectric material, and the like, and has a high etching

selectivity between a gap filling material composition and the photoresist, and a gap filling material composition and a bottom anti reflective coating layer. . Therefore, the gap filling material composition simplifies a process, and prevents waste of cost through omitting an unnecessary process.

WHAT IS CLAIMED IS:

1. A copolymer for a gap filling material, as expressed in Chemical Formula 1 below,

[Chemical Formula 1]

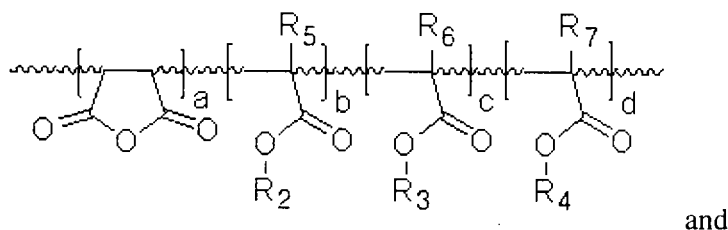


wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are independent from each other, R_1 is hydrogen or a C1-10 alkyl group, each of R_2 , R_3 , and R_4 indicates hydrogen, the C1-10 alkyl group, or a C1-20 arylalkyl group, each of R_5 , R_6 , and R_7 indicates hydrogen or a methyl group, and each of a, b, c, and d is a number indicating a repeating unit in a main chain, where $a+b+c+d = 1$, $0.05 < a/(a+b+c+d) < 0.95$, $0.05 < b/(a+b+c+d) < 0.95$, $0.05 < c/(a+b+c+d) < 0.95$, and $0.05 < d/(a+b+c+d) < 0.95$.

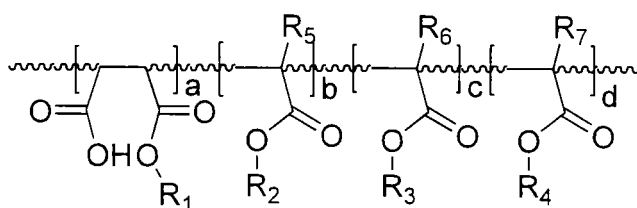
2. A method of manufacturing a copolymer for a gap filling material, the method comprising:

performing polymerization of a maleic acid anhydride and an acrylate compound to generate a first polymer as expressed in Chemical Formula 2 below; and
performing reaction of the first copolymer and C1-10 alkyl alcohol to generate a second copolymer as expressed in Chemical Formula 3 below,

[Chemical Formula 2]



[Chemical Formula 3]



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are independent from each other, R_1 is hydrogen or a C1-10 alkyl group, each of R_2 , R_3 , and R_4 indicates hydrogen, the C1-10 alkyl group, or a C1-20 arylalkyl group, each of R_5 , R_6 , and R_7 indicates hydrogen or a methyl group, and each of a, b, c, and d is a number indicating a repeating unit in a main chain, where $a+b+c+d = 1$, $0.05 < a/(a+b+c+d) < 0.95$, $0.05 < b/(a+b+c+d) < 0.95$, $0.05 < c/(a+b+c+d) < 0.95$, and $0.05 < d/(a+b+c+d) < 0.95$.

3. The method of claim 2, wherein the acrylate compound is at least one selected from a group consisting of methyl acrylate, ethyl acrylate, isopropyl acrylate, n-propyl acrylate, n-butyl acrylate, isobornyl acrylate, 2-ethylhexyl acrylate, methyl methacrylate, ethyl methacrylate, isopropyl methacrylate, n-propyl methacrylate, tert-butyl methacrylate, n-butyl methacrylate, isobutyl methacrylate, cyclohexyl methacrylate, isobornyl methacrylate, diethylene glycol monomethyl ether methacrylate, 2-ethylhexyl methacrylate, benzyl methacrylate, 1-naphthylmethyl methacrylate, 2-naphthylmethyl methacrylate, 9-anthrylmethyl methacrylate, 1-anthrylmethyl methacrylate, and 2-anthrylmethyl methacrylate.

4. The method of claim 2, wherein the polymerization is at least one of a bulk polymerization, a solution polymerization, a suspension polymerization, a bulk-suspension polymerization, an emulsion polymerization, and a radical polymerization.

5

5. The method of claim 4, wherein an initiator for the radical polymerization is at least one selected from a group consisting of azobisisobutyronitrile, benzoyl peroxide, lauryl peroxide, azobisiso capronitrile, azobisisovaleronitril, and t-butyl hydroperoxide.

10

6. The method of claim 4, wherein a polymerization solvent for the radical polymerization is at least one selected from a group consisting of benzene, toluene, xylene, halogenated benzene, diethyl ether, tetrahydrofuran, esters, ethers, lactones, ketones, amides.

15

7. The method of claim 2, wherein a weight-averaged molecular weight in terms of polystyrene through a gel permission chromatography is about 1,000 to about 100,000.

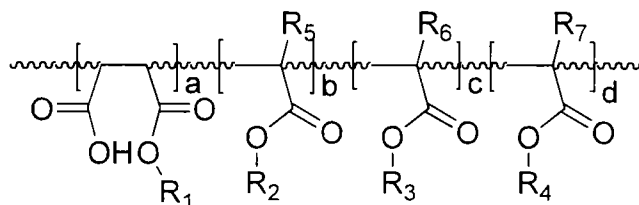
20

8. The method of claim 2, wherein a molecular weight distribution of the first polymer is about 1.0 to about 5.0.

9. A gap filling material composition, the composition comprising a light-absorptive material, a thermal acid generator, a crosslinking agent, and a copolymer for

the gap filling material composition as expressed in Chemical Formula 4 below,

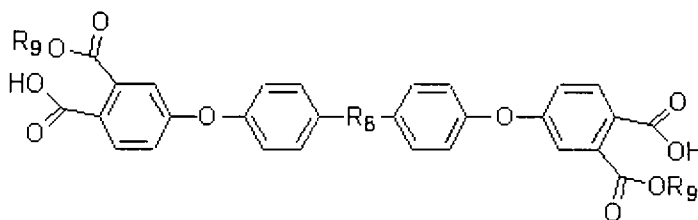
[Chemical Formula 4]



wherein R_1 , R_2 , R_3 , R_4 , R_5 , R_6 , and R_7 are independent from each other, R_1 is hydrogen or a C1-10 alkyl group, each of R_2 , R_3 , and R_4 indicates hydrogen, the C1-10 alkyl group, or a C1-20 arylalkyl group, each of R_5 , R_6 , and R_7 indicates hydrogen or a methyl group, and each of a , b , c , and d is a number indicating a repeating unit in a main chain, where $a+b+c+d = 1$, $0.05 < a/(a+b+c+d) < 0.95$, $0.05 < b/(a+b+c+d) < 0.95$, $0.05 < c/(a+b+c+d) < 0.95$, and $0.05 < d/(a+b+c+d) < 0.95$

10. The gap filling material composition of claim 9, wherein the light-absorptive material includes a monomer-typed light-absorptive material as expressed in Chemical Formulas 5 and 6 below,

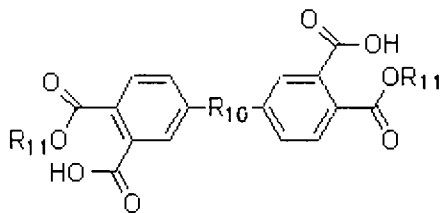
[Chemical Formula 5]



wherein R_8 is $-O-$, $-SO_2-$, $-C(CH_3)_2-$ or $-C(=O)-$, and R_9

independently indicates hydrogen, C1-10 alkyl, or C1-10 alkoxy, and

[Chemical Formula 6]



wherein R_{10} is $—O—$, $—S(=O)_2—$, $—C(CH_3)_2—$ or $—C(=O)—$, and R_{11}

independently indicates hydrogen, C1-10 alkyl, or C1-10 alkoxy.

5

11. The gap filling material composition of claim 9, wherein the crosslinking agent is a compound containing at least two crosslinking functional groups, and is at least one selected from a group consisting of an aminoplastic compound, a multi-functional epoxy resin, an anhydride, and a mixture thereof.

10

12. The gap filling material composition of claim 9, wherein the crosslinking agent is at least one selected from a group consisting of oxetanyl, oxazolin, cyclocarbonate, alcohol silyl, aminomethylol, alkoxymethyl, aziridinyl, methylol, isocyanate, alkoxymethylamino, and multifunctional epoxy.

15

13. The gap filling material composition of claim 11, wherein the aminoplastic compound is at least one selected from a group consisting of dimethoxymethylglycouril, diethoxymethylglycouril, a mixture of dimethoxymethylglycouril and diethoxymethylglycouril,

diethyldimethylmethylglycouril, tetramethoxymethylglycouril, and hexamethoxymethyl melamine resin.

14. The gap filling material composition of claim 9, wherein the thermal
5 acid generator is at least one selected from a group consisting of toluenesulfonic acid, amine salt of toluenesulfonic acid, pyridine salt of toluenesulfonic acid, alkylsulfonic acid, amine salt of alkylsulfonic acid, and pyridine salt of alkylsulfonic acid.

15. The gap filling material composition of claim 9, wherein an organic
10 solvent used for manufacturing the gap filling material composition is at least one selected from a group consisting of propylene glycol monomethyl ether (PGME), propylene glycol monomethyl ether acetate (PGMEA), cyclohexanone, ethyl lactate, propylene glycol n-propyl ether, dimethylformamide (DMF), γ -butyrolactone, ethoxy ethanol, methoxy ethanol, methyl 3-methoxy propionate (MMP), and ethyl 3-
15 ethoxypropionate (EEP).

16. The gap filling material composition of claim 9, wherein the gap filling material composition comprises;

about 0.1 w% to about 30 w% of the copolymer for the gap filling material
20 composition;

about 0.1 w% to about 50 w% of the light-absorptive material;

about 0.01 w% to about 30 w% of the thermal acid generator; and

about 0.01 w% to about 25 w% of the crosslinking agent.