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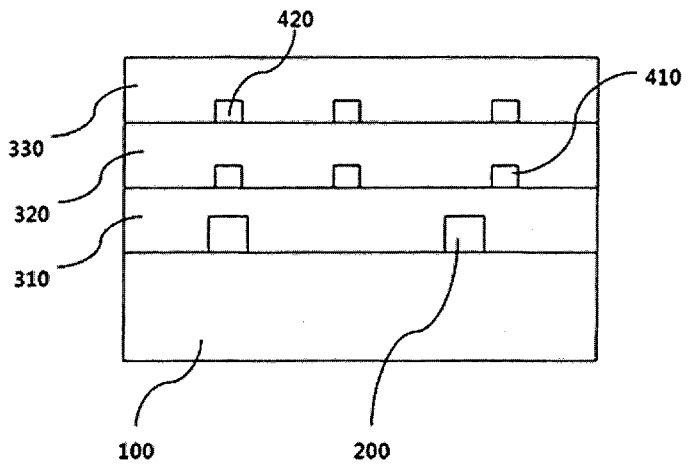
[Continued on next page]

(54) Title: COMPOSITION HAVING HIGH HEAT- AND CHEMICAL-RESISTANCE AND METHOD FOR PREPARING PROTECTIVE THIN FILM USING SAME

FIG. 1



(57) Abstract: The present invention relates to a composition comprising an aromatic compound having high heat- and chemical-resistance and a method for preparing a protective thin film using same. The protective thin film prepared from the inventive composition is capable of maintaining its physical shape with no thermal deformation even when exposed to high heat of 300C or greater, shows excellent chemical resistance against an acid, a base or an organic solvent, and maintains the shape of an exposed surface during plasma treatment, thereby effectively functioning as a protective thin film for the protection of an underlying material.

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DESCRIPTION

COMPOSITION HAVING HIGH HEAT- AND CHEMICAL-RESISTANCE AND METHOD FOR PREPARING PROTECTIVE THIN FILM USING SAME

FIELD OF THE INVENTION

The present invention relates to a composition comprising an aromatic compound having high heat- and chemical-resistance and a method for preparing a protective thin film using same. Specifically, the present invention relates to a composition for forming a protective thin film for the protection against high heat, chemical exposure, and the like, more specifically, it relates to a composition for forming a protective thin film for the protection of an underlying material and selective chemical treatment.

BACKGROUND OF THE INVENTION

Conventionally, organic synthetic materials used for forming an overcoat film, a dielectric material or a protective thin film in a display device or semiconductor device are mostly acryl- or imide-based compositions (*see* US 2010/0147564 A1). Acryl-based compositions can be synthesized easily and show excellent overall processability and coating performance when applied in a device. However, there are some limitations in their properties such as anti-heat, anti-chemical, and the like. Whereas imide-based compositions show excellent properties such as anti-heat, anti-chemical and the like, but, synthetic method and production method thereof are difficult and there are some limitations in choosing a solvent because of their low solubilities.

Accordingly, the present inventors have endeavored to discover an aromatic compound having excellent heat resistance, solubility and chemical resistance which can be easily synthesized, and completed the present invention by obtaining a curable resin material useful for forming an overcoat film, a dielectric material or a protective thin film by employing the aromatic compound.

SUMMARY OF THE INVENTION

Therefore, it is an object of the present invention to provide a composition

having excellent heat resistance, solubility and chemical resistance. The composition may be used in semiconductor preparing processes. Particularly, the composition may be a composition for forming a protective thin film.

It is another object of the present invention to provide a method for forming a protective thin film by employing the composition.

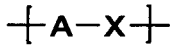
It is still another object of the present invention to provide a protective thin film obtained from the composition.

It is still another object of the present invention to provide a semiconductor device comprising the composition.

It is still another object of the present invention to provide a method for preparing the semiconductor device.

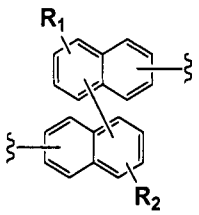
According to one aspect of the present invention, there is provided a composition comprising an aromatic compound having at least one of a repeating unit of Formula 1 and a repeating unit of Formula 2:

[Formula 1] [Formula 2]

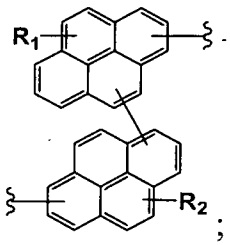


wherein,

A is any one selected from the group consisting of Formulae (a-1) to (a-4) represented by the following structural formulae:

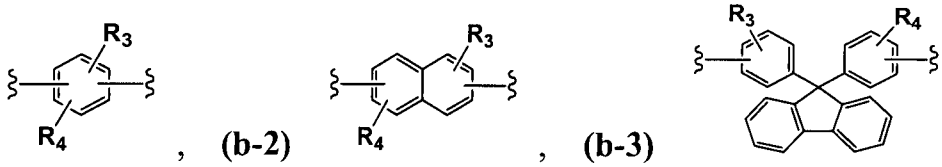


(a-1) , **(a-2)** , **(a-3)** , and **(a-4)**

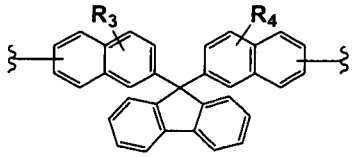


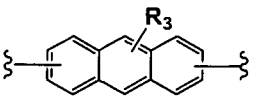
;

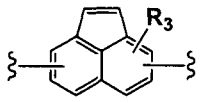
B is any one selected from the group consisting of Formulae (b-1) to (b-8) represented by the following structural formulae:



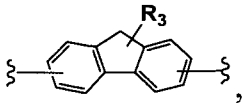
(b-1) , **(b-2)** , **(b-3)** , **(b-4)**

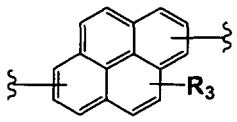


, **(b-5)** 

, **(b-6)** 

, **(b-7)**

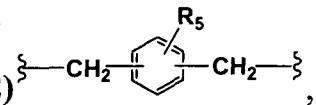


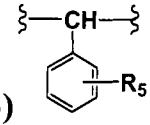
, and **(b-8)** 

;

X is any one selected from the group consisting of Formulae (c-1) to (c-3) represented by the following structural formulae:

(c-1)

, **(c-2)** 

, and **(c-3)** 

;

R_1, R_2, R_3, R_4, and R_5 are each independently hydrogen, hydroxy, -OR (wherein R is C_{1-10} alkyl or C_{6-10} aryl), C_{1-5} alkyl, C_{6-10} aryl, nitro, -NR'R" (wherein R' and R" are each independently hydrogen or C_{1-5} alkyl) or halogen.

According to another aspect of the present invention, there is provided a method for preparing a protective thin film comprising coating the inventive composition onto a substrate, followed by a heat treatment.

According to still another aspect of the present invention, there is provided a protective thin film obtained from the inventive composition.

According to still another aspect of the present invention, there is provided a semiconductor device comprising the inventive composition.

According to still another aspect of the present invention, there is provided a method for preparing a semiconductor device comprising the steps of:

(1) forming an etch target layer on a semiconductor substrate;

(2) forming a mask pattern on the etch target layer; and

(3) etching the etch target layer by using the mask pattern,

wherein the mask pattern is obtained from the inventive composition.

A protective thin film obtained from the composition according to the present invention is capable of maintaining its physical shape with no thermal deformation even when exposed to high heat of 300°C or greater, shows excellent chemical resistance against an acid, a base or an organic solvent, and maintains the shape of an exposed surface during plasma treatment. Therefore, the protective thin film can effectively function as a protective thin film for the protection of an underlying material.

BRIEF DESCRIPTION OF THE DRAWINGS

The above and other objects and features of the present invention will become apparent from the following description of the invention, when taken in conjunction with the accompanying drawings, which show:

FIG. 1: a cross-sectional view illustrating a semiconductor device comprising a dielectric layer obtained from the composition according to one embodiment of the present invention; and

FIG. 2: cross-sectional views illustrating a semiconductor device in each preparing processes according to one embodiment of the present invention.

<EXPLANATION OF THE REFERENCE NUMERALS>

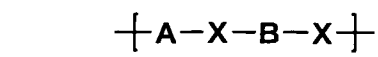
100: semiconductor substrate,	200: device element,
310: first interlayer dielectric film,	320: second interlayer dielectric film,
330: third interlayer dielectric film,	410: first wiring layer,
420: second wiring layer,	500: target device pattern,
501: etch target layer,	600: mask pattern,
601: mask layer,	700: photoresist pattern

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a composition comprising an aromatic compound having at least one of a repeating unit of Formula 1 and a repeating unit of Formula 2 as shown above. According to one embodiment of the present invention, the aromatic compound may comprise a repeating unit of Formula 1. According to another embodiment of the present invention, the aromatic compound may comprise a repeating unit of Formula 1 and a repeating unit of Formula 2.

According to another embodiment of the present invention, the aromatic compound may comprise a repeating unit of Formula 3:

[Formula 3]



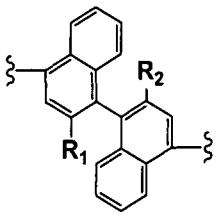
wherein A, B and X are the same as defined in Formulae 1 and 2 above.

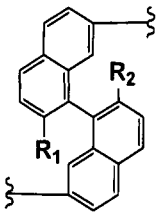
The aromatic compound may be an oligomer or a polymer comprising the aforementioned repeating units.

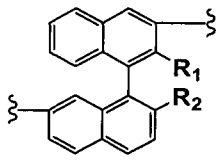
A substituent or a linker as shown in Formulae (a-1) to (a-4), Formulae (b-1)

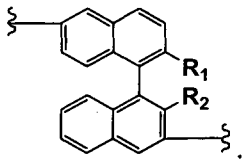
to (b-8) and Formulae (c-1) to (c-3) may be substituted at or linked to any carbon that is capable of substitution or forming a link.

For example, Formula (a-1) may comprise Formulae (i) to (iv) below:

(i) 

, (ii) 

, (iii) 

, and (iv) 

.

In Formulae 1 and 3, **A** is any one selected from the group consisting of Formulae (a-1) to (a-4) above. According to one embodiment, **A** is Formula (a-1) or (a-2). According to another embodiment, **A** is Formula (a-1).

In Formulae (a-1) to (a-4), R_1 and R_2 are each independently hydrogen, hydroxy, -OR (wherein, R is C_{1-10} alkyl or C_{6-10} aryl), C_{1-5} alkyl, C_{6-10} aryl, nitro, -NR'R" (wherein, R' and R" are each independently hydrogen or C_{1-5} alkyl) or halogen. According to one embodiment, R_1 and R_2 are each independently hydrogen, hydroxy or -OR (wherein, R is C_{1-10} alkyl or C_{6-10} aryl). According to another embodiment, R_1 is hydrogen, hydroxy or $-OCH_3$; R_2 is hydrogen, hydroxy, $-NH_2$ or $-OCH_3$. According to still another embodiment, R_1 and R_2 are each independently hydrogen or hydroxy. According to still another embodiment, R_1 and R_2 are hydroxy.

In Formulae 2 and 3, **B** is any one selected from the group consisting of Formulae (b-1) to (b-8) above. According to one embodiment, **B** is any one selected from the group consisting of Formulae (b-1), (b-5), (b-6), (b-7) and (b-8). According to another embodiment, **B** is any one selected from the group consisting of Formulae (b-1), (b-2), (b-3) and (b-4).

In Formulae (b-1) to (b-8), R_3 and R_4 are each independently hydrogen, hydroxy, -OR (wherein, R is C_{1-10} alkyl or C_{6-10} aryl), C_{1-5} alkyl, C_{6-10} aryl, nitro, -NR'R" (wherein, R' and R" are each independently hydrogen or C_{1-5} alkyl) or halogen. According to one embodiment, R_3 and R_4 are each independently hydrogen or hydroxy.

In Formulae 1 to 3, **X** is any one selected from the group consisting of

Formulae (c-1) to (c-3) above. According to one embodiment, **X** is Formula (c-1).

In Formulae (c-1) to (c-3), R_5 is hydrogen, hydroxy, -OR (wherein, R is C_{1-10} or C_{6-10} aryl), C_{1-5} alkyl, C_{6-10} aryl, nitro, -NR'R" (wherein, R' and R" are each independently hydrogen or C_{1-5} alkyl) or halogen. According to one embodiment, R_5 is hydrogen or hydroxy. According to another embodiment, R_5 is hydrogen.

The aromatic compound may comprise a repeating unit (Ra) of Formula 1 and a repeating unit (Rb) of Formula 2 in a molar ratio (Ra:Rb) of 0.01:0.99 to 0.99:0.01. According to one embodiment, the molar ratio of the repeating units (Ra:Rb) may be 0.1:0.9 to 0.9:0.1. According to another embodiment, the molar ratio of the repeating units (Ra:Rb) may be 0.4:0.6 to 0.6:0.4. According to still another embodiment, the molar ratio of the repeating units (Ra:Rb) may be 0.5:0.5.

The aromatic compound may be obtained by subjecting a compound comprising a moiety **A** and/or a compound comprising a moiety **B** with 1,3,5-trioxane, 1,4-bismethoxymethylbenzene or benzaldehyde to a coupling reaction in an organic solvent under conventional reaction conditions, and preferably an acid (for example, toluenesulfonic acid) may be added. During the coupling reaction above, bonds (links) may be formed among moieties **A** and/or moieties **B** at various carbon positions due to characteristics of aromatic moieties.

The aromatic compound may have a weight average molecular weight of 1,000 to 50,000, for example, 1,000 to 20,000, more specifically 1,000 to 10,000.

The aromatic compound not only shows excellent heat resistance by demonstrating at least 93% of a residue weight (wt%) in high heat conditions of 350°C or more, but also exhibits excellent solubility and completely dissolves in various organic solvents (see Experimental Examples 1 and 2).

The composition of the present invention may further comprise, besides the aromatic compounds, a solvent selected from the group consisting of cyclohexanone, propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monoethyl ether (PGME), ethyl lactate, γ-butyrolactone (GBL), *N*-methyl-1,2-pyrrolidone (NMP), chloroform, toluene, and a mixture thereof.

The composition of the present invention may comprise the aromatic compound in an amount of 0.1 to 30 wt% and a solvent in an amount of 70 to 99.9 wt% based on the total weight of the composition.

Further, the present invention provides a method for preparing a protective

thin film comprising coating the composition onto a substrate, followed by a heat treatment.

Any conventional coating methods well known in the art, for example, spin-on-coating, slit coating, bar coating or spray coating, may be used in the method for preparing a protective thin film.

The thickness of coating or condition of the heat treatment of the composition is not specifically limited. However, the composition may be coated on a substrate in a thickness of 10 nm to 5 μm, and then the heat treatment may be carried out at a temperature of 200°C to 600°C, preferably 240°C to 400°C for 1 to 5 minutes to obtain a protective thin film.

The protective thin film thus prepared may have a thickness of 5 nm to 5,000 nm, preferably 10 nm to 3,000 nm, more preferably 50 nm to 500 nm.

According to one embodiment of the present invention, the composition of the present invention may be coated by a spin coating method, and the heat treatment may be carried out at 350°C for 2 minutes, thereby forming a protective thin film with a thickness of about 350 nm.

Further, the present invention provides a protective thin film obtained from the composition.

According to one embodiment of the present invention, the protective thin film obtained from the composition of the present invention can maintain its overall physical shape well. In addition, the thin film shows excellent chemical resistance, so the thin film and the thickness thereof do not change even after being exposed to an acid, a base, an organic solvent, etc.; and exhibits a slow degradation even during a plasma etching process (when exposed to plasma), and undesirable phenomena such as cracking or peeling of the film after the etching process can be prevented (*see* Experimental Examples 3 to 5).

Accordingly, the protective thin film of the present invention may be applied for surface treatment of metallic components in machines, a packing material of electronic product, and a protective thin film used in a display device or semiconductor process. More specifically, the protective thin film may be used in preparing processes of a flat screen display device or a semiconductor device as an overcoat film for planarization, a protective meterial, a dielectric material, a dielectric film or a mask for selective treatment of an underlying layer.

Further, the present invention provides a protective thin film obtained from the composition, specifically, a semiconductor device comprising the protective thin

film.

Specifically, the present invention provides a semiconductor device, which comprises a dielectric film comprising an aromatic compound having at least one of a repeating unit of Formula 1 and a repeating unit of Formula 2 (wherein, A, B and X in Formulae 1 and 2 are the same as defined above).

More specifically, with reference to FIG. 1, a semiconductor device according to one embodiment may comprises a semiconductor substrate (100), a device element (200), interlayer dielectric layers (310, 320, and 330), and wiring layers (410 and 420).

The semiconductor substrate (100) may be a silicon substrate. The semiconductor substrate (100) may comprise a dielectric layer such as a silicon oxide layer, etc.

The device element (200) is formed on the semiconductor substrate (100). The device element may be a transistor, an image sensor or a capacitor.

Interlayer dielectric films (310, 320 and 330) are formed on the semiconductor substrate (100). For example, a first interlayer dielectric film (310) is formed on the semiconductor substrate (100). The first interlayer dielectric film (310) is disposed on the device element (200).

Also, a second interlayer dielectric film (320) is formed on the first interlayer dielectric film (310). The second interlayer dielectric film (320) is disposed on a first wiring layer (410).

A third interlayer dielectric film (330) is formed on the second interlayer dielectric film (320). The third interlayer dielectric film (330) is disposed on a second wiring layer (420).

The first wiring layer (410) is disposed on the first interlayer dielectric film (310). The first wiring layer (410) is connected to the device element (200).

The second wiring layer (420) is disposed on the second interlayer dielectric film (320). The second wiring layer (420) is connected to the device element (200) and/or the first wiring layer (410).

The first interlayer dielectric film (310), the second interlayer dielectric film (320) and the third interlayer dielectric film (330) may comprise a composition according to the examples as described above or examples which will be described below.

More specifically, in order to form the first interlayer dielectric film (310), the device element (200) are formed on the semiconductor substrate (100) and then the composition according to the examples of the present invention are coated

thereon. The composition may be coated by using conventional coating methods such as spin-on-coating, slit coating, bar coating, spray coating, and the like.

Subsequently, the composition thus coated is cured by a heat treatment process and the like, thereby forming the first interlayer dielectric film (310).

In similar manner, the second interlayer dielectric film (320) and the third interlayer dielectric film (330) may be formed.

Further, the present invention provides a method for preparing a semiconductor device comprising the steps of: forming an etch target layer on a semiconductor substrate; forming a mask pattern layer on the etch target layer; and etching the etch target layer by using the mask pattern layer, wherein the mask pattern layer comprises a composition according to the present invention, *i.e.*, a composition comprising an aromatic compound having at least one of a repeating unit of Formula 1 and a repeating unit of Formula 2 (wherein, A, B and X in Formulae 1 and 2 are the same as defined above).

As illustrated in FIG. 2, a semiconductor device may be prepared by using a composition according to the examples of the present invention.

With reference to (a) of FIG. 2, an etch target layer (501) is formed on a semiconductor substance (100). The etch target layer (501) may be a metal or silicon layer.

With reference to (b) of FIG. 2, a mask layer (601) is formed on the etch target layer (501). The mask layer (601) may comprise a composition according to the examples of the present invention. More specifically, the composition is coated on the etch target layer (501). Then, the composition thus coated is cured, and the mask layer is formed.

With reference to (c) of FIG. 2, a photoresist layer is formed on the mask layer (601), and the photoresist layer is subjected to a light exposure process and development process. As a result, the photoresist pattern (700) is formed on the mask layer (601).

With reference to (d) of FIG. 2, a pattern is formed on the mask layer (601) through the photoresist pattern (700). Thus, a mask pattern (600) is formed.

With reference to (e) FIG. 2, the etch target layer (501) is etched through the mask pattern (600), and the target device pattern (500) is formed on the semiconductor substrate (100).

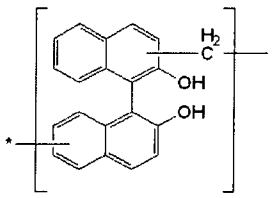
With reference to (f) of FIG. 2, the mask pattern (600) and the photoresist pattern (700) are removed. Subsequently, an additional layer may be formed on

the target device pattern (500), thereby forming a semiconductor device.

Thus, the mask pattern is formed by using the composition according to the examples of the present invention, and the semiconductor device is formed through the mask pattern.

Hereinafter, the present invention is described more specifically by following examples. However, these examples are provided only for illustration purposes, and the present invention is not limited thereto.

Example I-1: Synthesis of Aromatic Compound for Protective Thin Film



A 500 mL round-bottom three-neck flask was equipped with a thermometer, condenser, dropping funnel, and placed in a constant-temperature oil bath at 120°C. The oil bath was placed on a hot plate and introduced with a magnetic stirrer for stirring. The temperature of the cooling water of the condenser was kept at 10°C.

63.0 g of 1,1'-bi-2-naphthol (0.22 mol) and 25.8 g of 1,3,5-trioxane (0.286 mol) were dissolved in 212 g of cyclohexanone as a solvent in the three-neck flask. Subsequently, 2.1 g of p-toluenesulfonic acid monohydrate (11 mmol) was added thereto, and the mixture was stirred for 12 hours to carry out a reaction. The reaction temperature was maintained at 120°C.

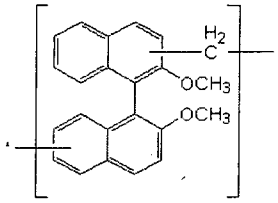
During the reaction, the reaction mixture was sampled and the weight average molecular weight of the sample was measured. The reaction was terminated by slowly cooling the reactant at room temperature when its weight average molecular weight reached a desired level.

600 g of a mixed solution of n-hexane and ethanol in a weight ratio of 80:20 was prepared, and the reactant obtained above was added dropwise, under stirring, into the solution. A supernatant formed from the reaction was discarded, and a polymer aggregate formed on the bottom of the flask was separated. Subsequently, the aggregate was dried in a vacuum oven at 80°C for 24 hours to eliminate the remaining solvent and impurities, and thus an aromatic compound was obtained in a powder form.

The aromatic compound thus obtained was analyzed by gel permeation chromatography (GPC) under a tetrahydrofuran (THF) solvent, and the result showed that the aromatic compound had a weight average molecular weight of

3,500 and a polydispersity (weight distribution) index of 1.9.

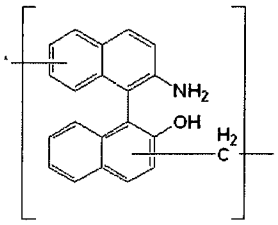
Example I-2: Synthesis of Aromatic Compound for Protective Thin Film



An aromatic compound was prepared by using the same procedure of Example I-1, except for using 63.0 g of 2,2'-dimethoxy-1,1-binaphthalene (0.2 mol) instead of 63.0 g of 1,1'-bi-2-naphthol (0.22 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 2,200 and a polydispersity index of 2.1.

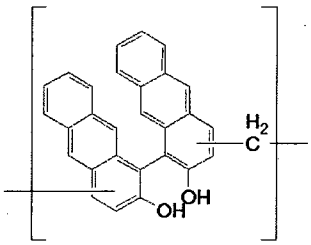
Example I-3: Synthesis of Aromatic Compound for Protective Thin Film



An aromatic compound was prepared by using the same procedure of Example I-1, except for using 62.8 g of 2-amino-2'-hydroxy-1,1'-binaphthyl (0.22 mol) instead of 63.0 g of 1,1'-bi-2-naphthol (0.22 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 1,900 and a polydispersity index of 2.2.

Example I-4: Synthesis of Aromatic Compound for Protective Thin Film



A 500 mL round-bottom three-neck flask was equipped with a thermometer, condenser, dropping funnel, and placed in a constant-temperature oil bath at 140°C. The oil bath was placed on a hot plate and introduced with a magnetic stirrer for

stirring. The temperature of the cooling water of the condenser was kept at 10°C.

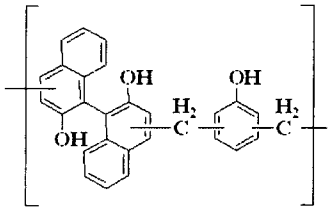
65.7 g of 2,2'-dihydroxy-1,1'-bianthracene (0.17 mol) and 19.9 g of 1,3,5-trioxane (0.22 mol) were dissolved in 207 g of cyclohexanone as a solvent in the three-neck flask. Subsequently, 3.23 g of p-toluenesulfonic acid monohydrate (17 mmol) was added thereto, and the mixture was stirred for 24 hours to carry out a reaction. The reaction temperature was maintained at 140°C.

During the reaction, the reaction mixture was sampled and the weight average molecular weight of the sample was measured. The reaction was terminated by slowly cooling the reactant at room temperature when its weight average molecular weight reached a desired level.

600 g of a mixed solution of n-hexane and ethanol in a weight ratio of 80:20 was prepared, and the reactant obtained above was added dropwise, under stirring, into the solution. A supernatant formed from the reaction was discarded, and a polymer aggregate formed on the bottom of the flask was separated. Subsequently, the aggregate was dried in a vacuum oven at 80°C for 24 hours to eliminate the remaining solvent and impurities, and thus an aromatic compound was obtained in a powder form.

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 1,700 and a polydispersity index of 2.4.

Example II-1: Synthesis of Aromatic Compound for Protective Thin Film



A 500 mL round-bottom three-neck flask was equipped with a thermometer, condenser, dropping funnel, and placed in a constant-temperature oil bath at 120°C. The oil bath was placed on a hot plate and introduced with a magnetic stirrer for stirring. The temperature of the cooling water of the condenser was kept at 10°C.

43.0 g of 1,1'-bi-2-naphthol (0.15 mol), 14.1 g of phenol (0.15 mol) and 35.1 g of 1,3,5-trioxane (0.39 mol) were dissolved in 222 g of cyclohexanone as a solvent in the three-neck flask. Subsequently, 2.85 g of p-toluenesulfonic acid monohydrate (15 mmol) was added thereto, and the mixture was stirred for 12 hours to carry out a reaction. The reaction temperature was maintained at 120°C.

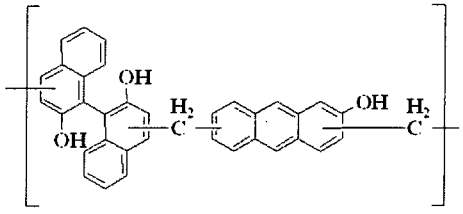
During the reaction, the reaction mixture was sampled and the weight

average molecular weight of the sample was measured. The reaction was terminated by slowly cooling the reactant at room temperature when its weight average molecular weight reached a desired level.

600 g of a mixed solution of n-hexane and ethanol in a weight ratio of 80:20 was prepared, and the reactant obtained above was added dropwise, under stirring, into the solution. A supernatant formed from the reaction was discarded, and a polymer aggregate formed on the bottom of the flask was separated. Subsequently, the aggregation was dried in a vacuum oven at 80°C for 24 hours to eliminate the remaining solvent and impurities, and thus an aromatic compound was obtained in a powder form.

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 5,500 and a polydispersity index of 1.8.

Example II-2: Synthesis of Aromatic Compound for Protective Thin Film



A 500 mL round-bottom three-neck flask was equipped with a thermometer, condenser, dropping funnel, and placed in a constant-temperature oil bath at 150°C. The oil bath was placed on a hot plate and introduced with a magnetic stirrer for stirring. The temperature of the cooling water of the condenser was kept at 10°C.

43.0 g of 1,1'-bi-2-naphthol (0.15 mol), 29.1 g of 2-hydroxyanthracene (0.15 mol) and 35.1 g of 1,3,5-trioxane (0.39 mol) were dissolved in 263 g of cyclohexanone as a solvent in the three-neck flask. Subsequently, 5.7 g of p-toluenesulfonic acid monohydrate (30 mmol) was added thereto, and the mixture was stirred for 20 hours to carry out a reaction. The reaction temperature was maintained at 150°C.

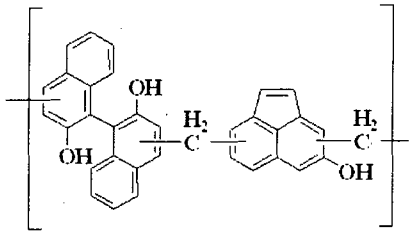
During the reaction, the reaction mixture was sampled and the weight average molecular weight of the sample was measured. The reaction was terminated by slowly cooling the reactant at room temperature when its weight average molecular weight reached a desired level.

600 g of a mixed solution of n-hexane and ethanol in a weight ratio of 80:20 was prepared, and the reactant obtained above was added dropwise, under stirring, into the solution. A supernatant formed from the reaction was discarded, and a

polymer aggregate formed on the bottom of the flask was obtained. Subsequently, the aggregate was dried in a vacuum oven at 80°C for 24 hours to eliminate the remaining solvent and impurities, and thus an aromatic compound was obtained in a powder form.

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 2,300 and a polydispersity index of 2.1.

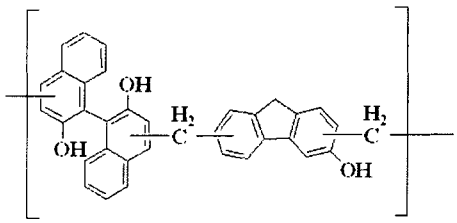
Example II-3: Synthesis of Aromatic Compound for Protective Thin Film



An aromatic compound was prepared by using the same procedure of Example II-2, except for using 25.2 g of 4-hydroxyacenaphthylene (0.15 mol) instead of 29.1 g of 2-hydroxyanthracene (0.15 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 2,800 and a polydispersity index of 2.0.

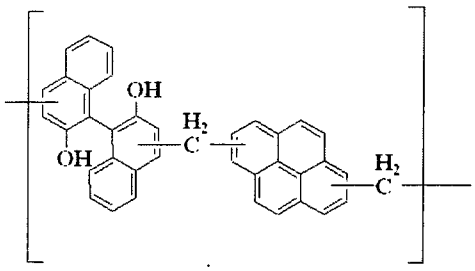
Example II-4: Synthesis of Aromatic Compound for Protective Thin Film



An aromatic compound was prepared by using the same procedure of Example II-2, except for using 27.3 g of 3-hydroxyfluorene (0.15 mol) instead of 29.1 g of 2-hydroxyanthracene (0.15 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 2,100 and a polydispersity index of 2.3.

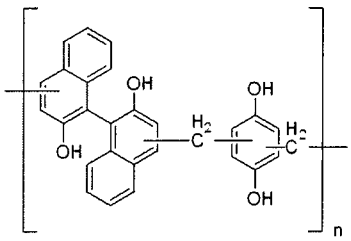
Example II-5: Synthesis of Aromatic Compound for Protective Thin Film



An aromatic compound was prepared by using the same procedure of Example II-1, except for using 30.3 g of pyrene (0.15 mol) instead of 14.1 g of phenol (0.15 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 3,200 and a polydispersity index of 1.9.

Example III-1: Synthesis of Aromatic Compound for Protective Thin Film



A 500 mL round-bottom three-neck flask was equipped with a thermometer, condenser, dropping funnel, and placed in a constant-temperature oil bath at 100°C. The oil bath was placed on a hot plate and introduced with a magnetic stirrer for stirring. The temperature of the cooling water of the condenser was kept at 10°C.

71.6 g of 1,1'-bi-2-naphthol (0.25 mol), 8.3 g of hydroquinone (0.075 mol) and 40.5 g of 1,3,5-trioxane (0.45 mol) were dissolved in 128 g of cyclohexanone as a solvent in the three-neck flask. Subsequently, 7.1 g of p-toluenesulfonic acid monohydrate (38 mmol) was added thereto, and the mixture was stirred to carry out a reaction. The reaction temperature was maintained at 100°C.

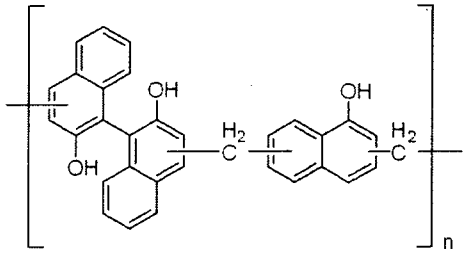
During the reaction, the reaction mixture was sampled and the weight average molecular weight of the sample was measured. The reaction was terminated by slowly cooling the reactant at room temperature when its weight average molecular weight reached a desired level.

800 g of a mixed solution of n-hexane and ethanol in a weight ratio of 80:20 was prepared, and the reactant obtained above was added dropwise, under stirring, into the solution. A supernatant formed from the reaction was discarded, and a polymer aggregate formed on the bottom of the flask was obtained. Subsequently, the aggregate was dried in a vacuum oven at 80°C for 24 hours to eliminate the

remaining solvent and impurities, and thus an aromatic compound was obtained in a powder form.

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 4,300 and a polydispersity index of 1.9.

Example III-2: Synthesis of Aromatic Compound for Protective Thin Film



A 500 mL round-bottom three-neck flask was equipped with a thermometer, condenser, dropping funnel, and placed in a constant-temperature oil bath at 130°C. The oil bath was placed on a hot plate and introduced with a magnetic stirrer for stirring. The temperature of the cooling water of the condenser was kept at 10°C.

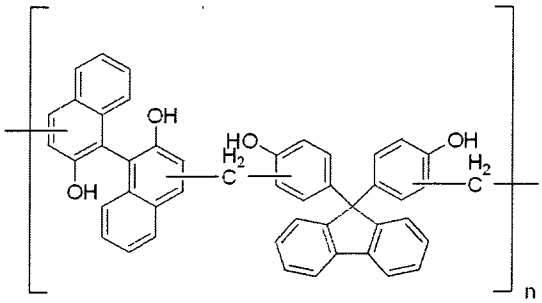
71.6 g of 1,1'-bi-2-naphthol (0.25 mol), 18.0 g of 1-naphthol (0.125 mol) and 40.5 g of 1,3,5-trioxane (0.45 mol) were dissolved in 137 g of cyclohexanone as a solvent in the three-neck flask. Subsequently, 7.1 g of p-toluenesulfonic acid monohydrate (38 mmol) was added thereto, and the mixture was stirred to carry out a reaction. The reaction temperature was maintained at 130°C.

During the reaction, the reaction mixture was sampled and the weight average molecular weight of the sample was measured. The reaction was terminated by slowly cooling the reactant at room temperature when its weight average molecular weight reached a desired level.

800 g of a mixed solution of n-hexane and ethanol in a weight ratio of 80:20 was prepared, and the reactant obtained was added dropwise, under stirring, into the solution. A supernatant formed from the reaction was discarded, and a polymer aggregate formed on the bottom of the flask was obtained. Subsequently, the aggregate was dried in a vacuum oven at 80°C for 24 hours to eliminate the remaining solvent and impurities, and thus an aromatic compound was obtained as a powder.

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 7,400 and a polydispersity index of 2.1.

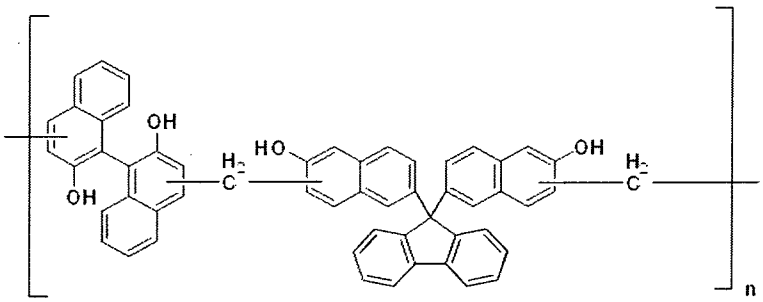
Example III-3: Synthesis of Aromatic Compound for Protective Thin Film



An aromatic compound was prepared by using the same procedure of Example III-2, except for using 43.8 g of 9,9-bis(4-hydroxyphenyl)fluorene (0.125 mol) instead of 18.0 g of 1-naphthol (0.125 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 5,800 and a polydispersity index of 2.1.

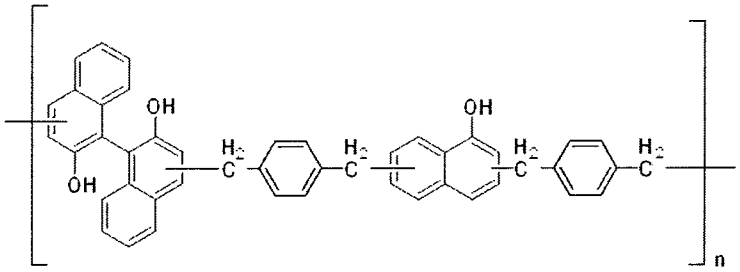
Example III-4: Synthesis of Aromatic Compound for Protective Thin Film



An aromatic compound was prepared by using the same procedure of Example III-2, except for using 56.3 g of 6,6'-(9H-fluorene-9,9-diyl)bis(naphthalen-2-ol) (0.125 mol) instead of 18.0 g of 1-naphthol (0.125 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 5,100 and a polydispersity index of 2.3.

Example III-5: Synthesis of Aromatic Compound for Protective Thin Film

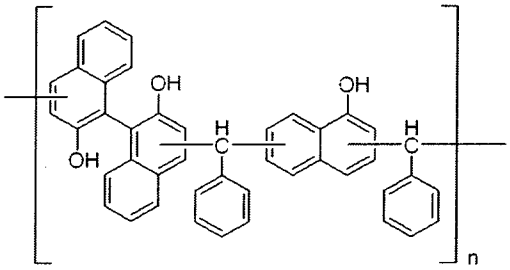


An aromatic compound was prepared by using the same procedure of

Example III-2, except for using 83.1 g of 1,4-bis(methoxymethyl)benzene (0.50 mol) instead of 40.5 g of 1,3,5-trioxane (0.45 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 3,800 and a polydispersity index of 1.9.

Example III-6: Synthesis of Aromatic Compound for Protective Thin Film



An aromatic compound was prepared by using the same procedure of Example III-2, except for using 53.1 g of benzaldehyde (0.50 mol) instead of 40.5 g of 1,3,5-trioxane (0.45 mol).

The aromatic compound thus obtained was analyzed by GPC under THF, and the result showed that the aromatic compound had a weight average molecular weight of 3,200 and a polydispersity index of 2.0.

Comparative Example I: Synthesis of Aromatic Compound for Protective Thin Film

An aromatic compound for protective thin film was prepared according to the method disclosed in US Patent Application Publication No. 2010/0147564 A1. Specifically, 3,4'-oxydianiline (3 mmol) was placed in a well-dried sealed reactor with a stirrer, and dissolved in 7.3 mL of dehydrated N-methyl-1,2-pyrrolidone (NMP). Subsequently, mellophanic dianhydride powder (3 mmol) was added to the resulting solution. The mixture thus obtained was stirred at room temperature for 3 hours to obtain a linear polyimide precursor solution that was transparent, uniform and viscous. The linear polyimide precursor solution was properly diluted to a concentration of 10 to 20 wt%, added dropwise with 10 mL of cyclodehydration reagent (acetic anhydride/pyridine = 7/3 by volume), and stirred at room temperature for 12 hours to carry out imidization. The polyimide solution thus obtained was added dropwise into a large amount of methanol, and then polyimide precipitates were collected and dried to obtain a polyimide as a powder.

Comparative Example II: Synthesis of Aromatic Compound for Protective

Thin Film

Polyimide powder was prepared by using the same procedure of Comparative Example I, except for using as a diamine component 2,2-bis(4-(4-aminophenoxy)phenyl)propane (BAPP) together with 4,4'-oxydianiline (4,4'-ODA), wherein the molar ratio (BAPP:4,4'-ODA) is 70:30, instead of using 3,4'-oxydianiline alone.

Experimental Example 1: Heat Resistance Evaluation

20 mg of each aromatic compound prepared in the examples and the comparative examples was weighed, and heat resistance of the compound was evaluated by using a thermogravimetric analyzer instrument (TF-DTA2000, Bruker AXS Inc.). Compounds were heated at a rate of 10°C/min under nitrogen, and the change in weight of each compound was measured. The results are shown in Table 1.

[Table 1]

Aromatic compound	Residual wt% (350°C, wt%)
Example I-1	96.5%
Example I-2	95.3%
Example I-3	93.2%
Example I-4	97.7%
Example II-1	96.7%
Example II-2	97.7%
Example II-3	94.5%
Example II-4	93.2%
Example II-5	96.0%
Example III-1	95.9%
Example III-2	97.6%
Example III-3	97.0%
Example III-4	97.8%
Example III-5	96.2%
Example III-6	94.2%
Comparative Example I	97.6%
Comparative Example II	95.8%

As shown in Table 1, the aromatic compounds of the examples had a residual weight of at least 93% at a high temperature of 350°C or more, thereby showing excellent heat resistance.

Experimental Example 2: Solubility Evaluation

0.5 g of each aromatic compound prepared in the examples and the comparative examples was placed in 5 g each of various solvents, and solubility of each aromatic compound at room temperature was analyzed. For this test, γ-butyrolactone (GBL), tetrahydrofuran, cyclohexanone (C.H), CP mixture (a mixture of cyclohexanone:PGMEA = 50:50, w/w), and propylene glycol monomethyl ether acetate (PGMEA) were used as the solvents. The results are shown in Table 2.

[Table 2]

Aromatic compound	GBL	THF	C.H	CP mixture	PGMEA
Example I-1	●	●	●	●	●
Example I-2	●	●	●	●	○
Example I-3	●	●	●	●	●
Example I-4	●	●	●	Δ	X
Example II-1	●	●	●	●	●
Example II-2	●	●	●	Δ	X
Example II-3	●	●	●	●	○
Example II-4	●	●	●	○	Δ
Example II-5	●	●	●	●	●
Example III-1	●	●	●	●	●
Example III-2	●	●	●	●	●
Example III-3	●	●	●	●	●
Example III-4	●	●	●	●	●
Example III-5	●	●	●	●	●
Example III-6	●	●	●	●	●
Comparative Example I	Δ	X	X	X	X
Comparative Example II	●	X	X	X	X

● : completely dissolved at room temperature,
○ : partially dissolved at room temperature, but completely dissolved when heated
Δ : partially dissolved when heated, X : insoluble

As shown in Table 2, the aromatic compounds prepared in the examples of the present invention exhibited good solubility in most solvents, the aromatic compounds of Comparative Examples I and II showed poor solubility.

Experimental Example 3: Formation of Thin Film

0.5 g of each aromatic compound prepared in the examples was dissolved in

4.5 g of cyclohexanone to prepare a sample solution (a composition for protective thin film). Each prepared sample solution was applied to an 8 inch silicon wafer by spin coating, and the silicon wafer was baked at 350°C for 2 minutes to form a thin film with a thickness of 300 nm.

Also, thin films were prepared by using the same procedure as above except that the aromatic compound powders prepared in the comparative examples were dissolved in NMP, instead of cyclohexanone. The results are shown in Table 3.

[Table 3]

Aromatic compound	Shape of Thin Film
Example I-1	Overall good shape (mirror surface and edges are good)
Example I-2	Same as above
Example I-3	Same as above
Example I-4	Same as above
Example II-1	Overall good shape (mirror surface and edges are good)
Example II-2	Same as above
Example II-3	Same as above
Example II-4	Same as above
Example II-5	Same as above
Example III-1	Overall good shape (mirror surface and edges are good)
Example III-2	Same as above
Example III-3	Same as above
Example III-4	Same as above
Example III-5	Same as above
Example III-6	Same as above
Comparative Example I	Center portion is good, but shrinkage is found at the edges
Comparative Example II	Center portion is good, but shrinkage is found at the edges

As shown in Table 3, the compositions comprising the aromatic compounds of the present invention exhibited a good shape of thin film, whereas the compositions comprising the aromatic compounds of Comparative Examples I and II had defects such as shrinkage at the edges.

Experimental Example 4: Chemical Resistance Evaluation of Thin Film

The thin film samples prepared in Experimental Example 3 by using the aromatic compounds of the examples and the comparative examples were submerged in an aqueous solution of HCl (HCl: water= 15:85 wt%), an aqueous solution of NaOH (NaOH: water= 15:85 wt%), cyclohexanone and propylene

glycol monomethyl ether acetate at room temperature for 2 minutes, and then the chemical resistance of the samples were evaluated by examining the changes in the shape and the thickness of the films. The results are shown in Table 4.

[Table 4]

Aromatic compound	Aqueous solution of HCl	Aqueous solution of NaOH	Cyclohexanone	PGMEA
Example I-1	○	○	○	○
Example I-2	○	○	○	○
Example I-3	○	○	○	○
Example I-4	○	○	○	○
Example II-1	○	○	○	○
Example II-2	○	○	○	○
Example II-3	○	○	○	○
Example II-4	○	○	○	○
Example II-5	○	○	○	○
Example III-1	○	○	○	○
Example III-2	○	○	○	○
Example III-3	○	○	○	○
Example III-4	○	○	○	○
Example III-5	○	○	○	○
Example III-6	○	○	○	○
Comparative Example I	○	○	○	○
Comparative Example II	○	○	○	○

○ : no changes in the shape can be detected by the naked eye, no changes in thickness
Δ : slight changes in the shape can be detected by the naked eye, change in thickness is 1 nm or less
X : changes in the shape and the thickness can be clearly detected by the naked eye

As shown in Table 4, the thin film samples prepared from the inventive aromatic compounds showed no change in the shape and the thickness of the film, thereby exhibiting good chemical resistance.

Experimental Example 5: Evaluation of the Shape of Thin Film after Etching

The thin film samples prepared in Experimental Example 3 by using the aromatic compounds of the examples and the comparative examples were subjected to plasma etching by employing a mixture of CH_2F_2/CF_4, and a degrading rate (film loss rate) of the thin films were measured. Also, any change in the shape of the thin films (for example, cracking or peeling of the thin film, etc.) was evaluated.

The results are shown in Table 5.

[Table 5]

Aromatic compound	Degrading rate (nm/s)	Shape after etching
Example I-1	3.6	Good
Example I-2	4.0	Good
Example I-3	4.3	Good
Example I-4	3.3	Good
Example II-1	3.8	Good
Example II-2	3.4	Good
Example II-3	3.7	Good
Example II-4	4.0	Good
Example II-5	3.3	Good
Example III-1	3.9	Good
Example III-2	3.4	Good
Example III-3	3.5	Good
Example III-4	3.2	Good
Example III-5	3.7	Good
Example III-6	4.1	Good
Comparative Example I	4.9	Good
Comparative Example II	5.3	Good

As shown in Table 5, the thin film samples prepared by using the aromatic compounds according to the examples exhibited slower etching rates as compared to those of the comparative examples, and maintained good shapes after the etching process without any defects such as cracking and peeling of the thin film. Based on the results above, a composition prepared from the aromatic compound of the present invention can effectively serve as a protective thin film or a mask for an underlying material during a plasma-applying process.

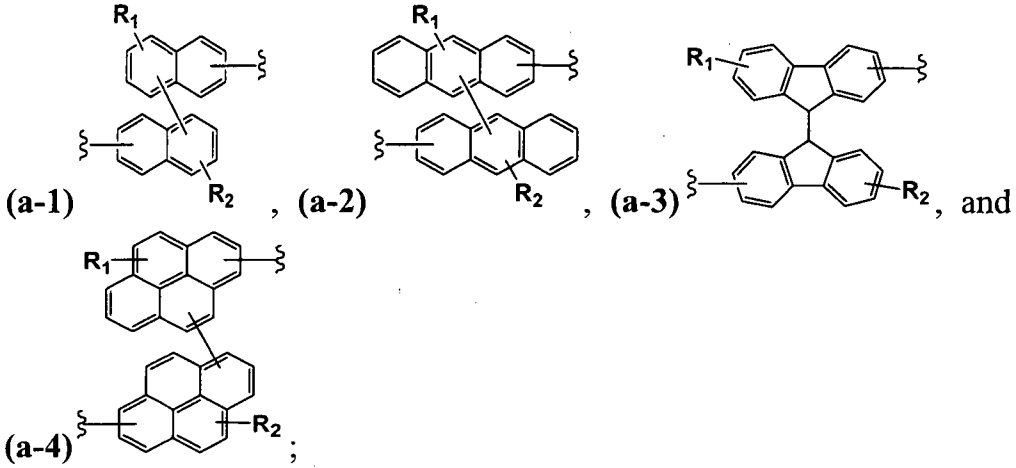
WHAT IS CLAIMED IS:

1. A composition comprising an aromatic compound having at least one of a repeating unit of Formula 1 and a repeating unit of Formula 2:

[Formula 1] [Formula 2]

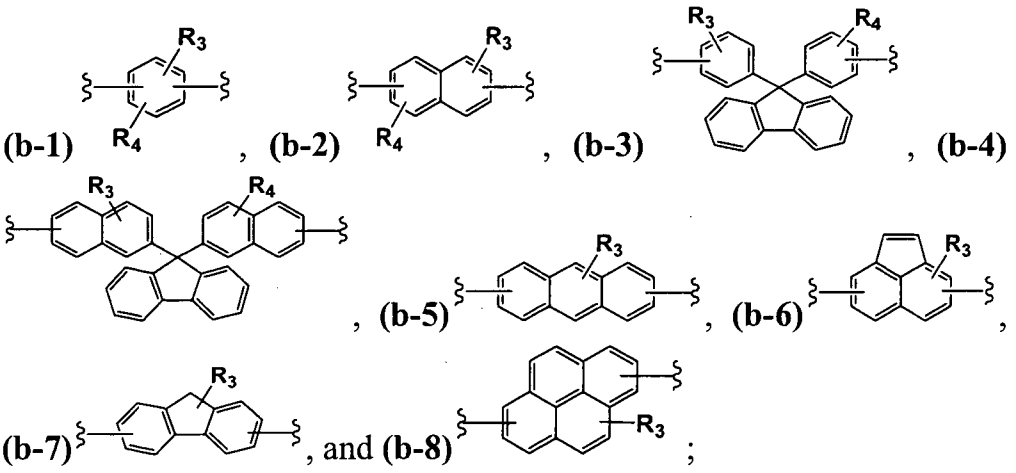
wherein,

A is any one selected from the group consisting of Formulae (a-1) to (a-4) represented by the following structural formulae:



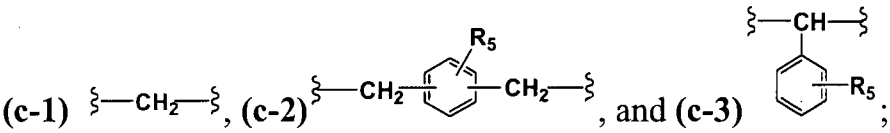
(a-1) , **(a-2)** , **(a-3)** , and **(a-4)** ;

B is any one selected from the group consisting of Formulae (b-1) to (b-8) represented by the following structural formulae:



(b-1) , **(b-2)** , **(b-3)** , **(b-4)** , **(b-5)** , **(b-6)** , **(b-7)** , and **(b-8)** ;

X is any one selected from the group consisting of Formulae (c-1) to (c-3) represented by the following structural formulae:



(c-1) , **(c-2)** , and **(c-3)** ;

R_1, R_2, R_3, R_4, and R_5 are each independently hydrogen, hydroxy, -OR

(wherein R is C_{1-10} alkyl or C_{6-10} aryl), C_{1-5} alkyl, C_{6-10} aryl, nitro, -NR'R" (wherein R' and R" are each independently hydrogen or C_{1-5} alkyl) or halogen.

2. The composition of claim 1, wherein the aromatic compound comprises a repeating unit of Formula 1.

3. The composition of claim 1, wherein **A** is Formula (a-1) or (a-2).

4. The composition of claim 3, wherein **A** is Formula (a-1).

5. The composition of claim 1, wherein **X** is Formula (c-1).

6. The composition of claim 1, wherein the aromatic compound comprises a repeating unit of Formula 1 (Ra) and a repeating unit of Formula 2 (Rb) in a molar ratio (Ra:Rb) of 0.01:0.99 to 0.99:0.01.

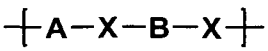
7. The composition of claim 6, wherein the molar ratio (Ra:Rb) of the repeating unit of Formula 1 (Ra) and the repeating unit of Formula 2 (Rb) is in a range of 0.4:0.6 to 0.6:0.4.

8. The composition of claim 1, wherein **B** is selected from the group consisting of Formulae (b-1), (b-5), (b-6), (b-7) and (b-8).

9. The composition of claim 1, wherein **B** is selected from the group consisting of Formulae (b-1), (b-2), (b-3) and (b-4).

10. The composition of claim 6, wherein the aromatic compound comprises a repeating unit of Formula 3:

[Formula 3]



wherein A, B and X are the same as defined in claim 1.

11. The composition of claim 1, wherein R_1 and R_2 are each independently hydrogen, hydroxy or -OR (wherein, R is C_{1-10} alkyl or C_{6-10} aryl).

12. The composition of claim 1, wherein R_1 is hydrogen, hydroxy or $-OCH_3$; R_2 is hydrogen, hydroxy, $-NH_2$ or $-OCH_3$; and R_3, R_4 and R_5 are each independently

hydrogen or hydroxy.

13. The composition of claim 12, wherein R_1, R_2, R_3, R_4 and R_5 are each independently hydrogen or hydroxy.

14. The composition of claim 1, wherein the aromatic compound has a weight average molecular weight of 1,000 to 50,000.

15. The composition of claim 1, wherein the composition further comprises a solvent selected from the group consisting of cyclohexanone, propylene glycol monomethyl ether acetate (PGMEA), propylene glycol monoethyl ether (PGME), ethyl lactate, γ-butyrolactone (GBL), *N*-methyl-1,2-pyrrolidone (NMP), chloroform, toluene, and a mixture thereof.

16. The composition of claim 15, wherein the composition comprises the aromatic compound in an amount of 0.1 to 30 wt% and a solvent in an amount of 70 to 99.9 wt% based on the total weight of the composition.

17. A method for preparing a protective thin film comprising coating the composition according to any one of claims 1 to 16 onto a substrate, followed by a heat treatment.

18. A protective thin film obtained from the composition according to any one of claims 1 to 16.

19. A semiconductor device comprising a dielectric layer obtained from the composition according to any one of claims 1 to 16.

20. A method for preparing a semiconductor device comprising the steps of:
forming an etch target layer on a semiconductor substrate;
forming a mask pattern on the etch target layer; and
etching the etch target layer by using the mask pattern,
wherein the mask pattern is obtained from the composition according to any one of claims 1 to 16.

FIG. 1

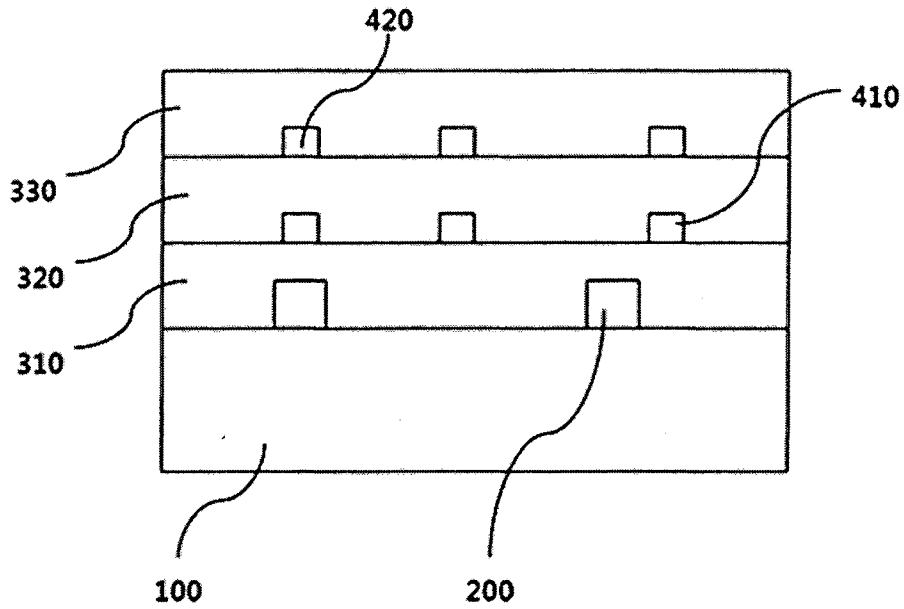
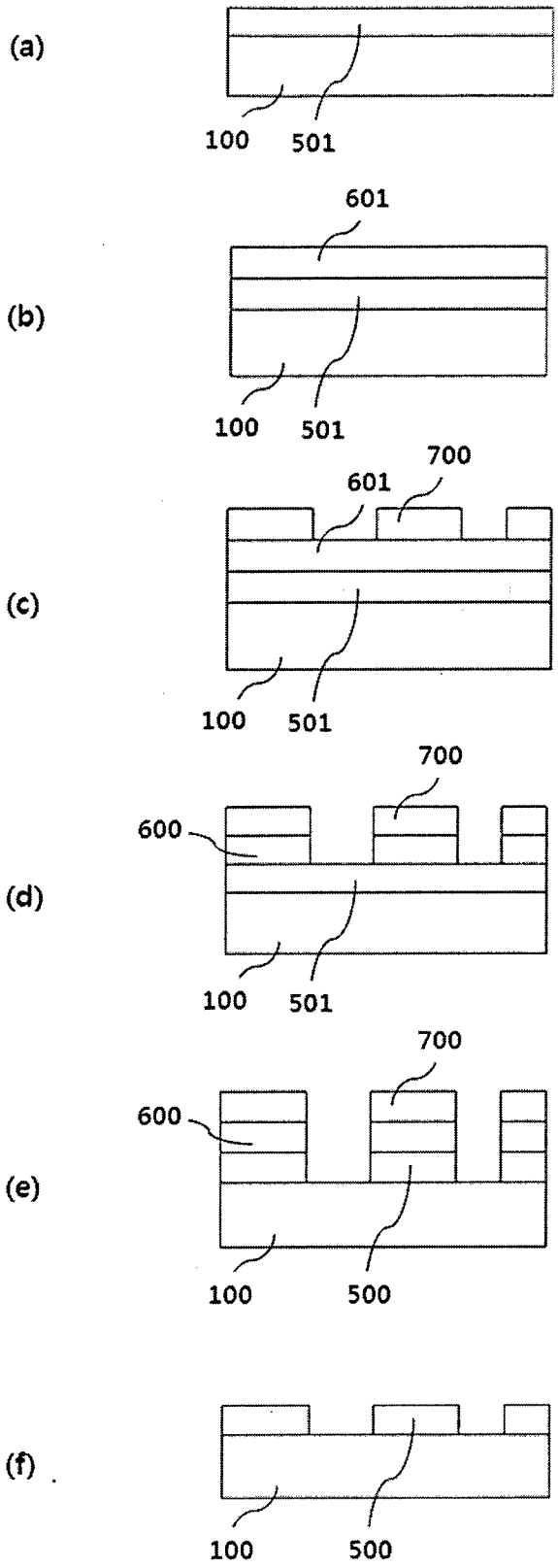


FIG. 2


(a)
100
501
(b)
601
100
501
(c)
700
601
100
501
(d)
700
600
100
501
(e)
700
600
100
500
(f)
100
500

INTERNATIONAL SEARCH REPORT

International application No.
PCT/KR2014/007066

A. CLASSIFICATION OF SUBJECT MATTER

C09D 7/12(2006.01)i, C09D 165/00(2006.01)i, C08L 65/00(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C09D 7/12; H01L 21/311; H01L 21/3105; G03C 1/00; G03C 1/494; C08G 8/02; C07C 39/17; C08L 61/12; B44C 1/22; C09D 165/02; C09D 165/00; C08L 65/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords:1,1-bi-2- naphthol, anthracene, pyrene, acenaphthylene, fluorene, tioxane

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 2006-0019195 A1 (JUN HATAKEYAMA et al.) 26 January 2006 See abstract; claims 2, 5; Paras. [48]-[51],[59],[133],[134],[152]	1-9,11-20
A		10
Y	US 2012-0064725 A1 (TAKESHI KINSHO et al.) 15 March 2012 See abstract; claims 4, 12; Para. [90]	1-9,11-20
A		10
A	US 2012-0184103 A1 (TSUTOMU OGIHARA et al.) 19 July 2012 See abstract; claim 1	1-20
A	US 2013-0087529 A1 (JUN HATAKEYAMA et al.) 11 April 2013 See abstract; claim 1; para.[145]	1-20
A	US 2012-0171868 A1 (TSUTOMU OGIHARA et al.) 05 July 2012 See abstract; claim 1	1-20
A	US 2007-0122740 A1 (JUN HATAKEYAMA et al.) 31 May 2007 See abstract; claim 1	1-20

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

* Special categories of cited documents:
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
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"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents,such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
13 November 2014 (13.11.2014)	**13 November 2014 (13.11.2014)**

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/KR2014/007066

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