

Description

Title of Invention: CURABLE COMPOSITION

TechnicalField

- [0001] The present invention relates to a curable composition, preferably being a photo-curable composition, method for preparing a curable composition, method for preparing a cured layer, a cured layer and a stacked layer.

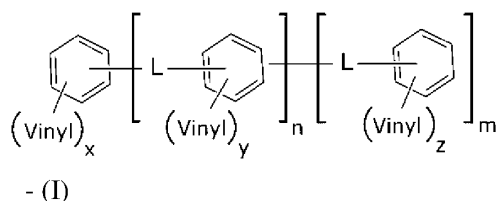
BackgroundArt

- [0002] Downscaling is an unbroken trend in the semiconductor industry to increase performance of microchips. However, achieving 7nm node technology and beyond significantly increases complexity and requires some new process and material solutions.
- [0003] Multilayer patterning processes play a prominent role in the transfer of fine lithography patterns to substrates and the importance will increase more and more as the industry reaches the next stages of development of advanced nodes.
- [0004] An underlayer Spin-on carbon (SOC) material with high etch resistance and good gap fill properties is a key material in these multilayer processes. As critical dimensions reach a few tens of nanometers, the existing topography becomes a major performance challenge. Reliable methods for planarizing such layers with classical chemical mechanical polishing (CMP) processes have not been established yet. New strategies to meet high levels of planarization are therefore of great interest to the industry.
- [0005] Inkjet Adaptive Planarization (IAP) processes can be used to planarize surfaces of substrates. For this purpose, liquid drops of a photocurable composition are printed on the surface of substrates. The drop pattern can be tailored to existing topographies. A flat superstrate is brought into direct contact with the liquid to form a flat layer of liquid. The flat liquid layer is typically cured under the influence of UV-light, and after removal of the superstrate, a planar surface is obtained, which can be subjected to subsequent processing steps.
- [0006] These cured layers can combine high etch resistance with high mechanical strength and good thermal stability that meet the requirements of hardmask materials for multilayer processes for the development of the next generation of microchips.
- [0007] State-of-the-art photocurable compositions usually contain a high content of acrylate monomers.
- [0008] US2020/0339828 A1 (Canon) claims, for example, the use of a photocurable composition comprising a polymerizable material and a photoinitiator, wherein at least 90wt% of the polymerizable material comprise acrylate monomers including an aromatic group; and a total carbon content of the photocurable composition after curing is at least 70%.

- [0009] US2021/0070906 A1 (Canon) covers the use of curable compositions that comprise a polymerizable material and an initiator, wherein the polymerizable material comprises a first monomer and a second monomer, the second monomer including a ring structure selected from a maleimide-ring, a pyrone ring, or a 2-furanone ring and where the second monomer is soluble in the first monomer, and the curable composition has a viscosity of lower 10 cP. In addition, the formulation can contain one further monomer that includes a substituted or unsubstituted divinyl benzene.
- [0010] US2021/0198400 A1 (Canon) deals with photocurable composition including 1,3-benzoxazine and acrylate monomers.
- [0011] US2022/0185914 A1 (Canon) describes a photocurable composition including the polymerizable material (divinylbenzene; in Examples) from about 15wt% to 85wt% and at least one multi-functional acrylate monomer from 15wt% to 85wt% based on the total weight of the photocurable composition (Examples, claims).
- [0012] In another piece of prior art literature (US2023/0203210 A1), polymerizable compositions based on vinylbenzene or alkyne containing bis aromatic systems are reported. The compositions can contain acrylates, as allowed by the subclaim of the reference.

Summary of Invention

- [0013] However, the inventors newly have found that there is still one or more of considerable problems for which improvement is desired, as listed below; improved thermal stability after curing, preferably at about 350°C or more; lower shrinkage after curing; improved etching resistance of a cured layer; improved planarization performance of a cured layer, namely over different pattern topographies of a substrate; lower viscosity and/or lower vapor pressure as a composition, preferably suitable for ink-jet printing.
- [0014] The inventors aimed to solve one or more of the above-mentioned problems.
- [0015] Then, the present inventors have surprisingly found that one or more of the above-described technical problems can be solved by the features as defined in the claims.
- [0016] Namely, it is found a novel curable composition, preferably being a photo-curable composition, comprising at least a 1st monomer compound, a 2nd monomer compound and a polymerization initiator, wherein said 1st monomer compound is represented by chemical formula (I):



wherein

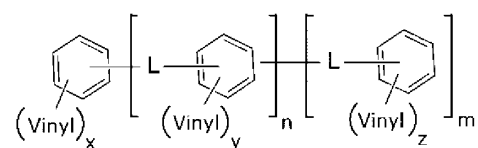
$$1 \leq x \leq 5, 0 \leq y \leq 4, 0 \leq z \leq 5;$$

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 ;

wherein said 2nd monomer compound is represented by chemical formula (I'), and the 1st monomer compound and the 2nd monomer compound are different of each other.



(I')

wherein

$$1 \leq x \leq 5, 0 \leq y \leq 4, 0 \leq z \leq 5;$$

n is 1 or 0, m is 1 or 0;

$1 \leq n+m \leq 2$ or $n+m$ can be 0 when x is $3 \leq x \leq 5$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 .

[0017] In another aspect, the present invention relates to a method for preparing the composition of the present invention, comprises at least the following step (A);

(A) Mixing at least a 1st monomer compound of formula (I), a 2nd monomer compound of formula (I') and a polymerization initiator.

[0018] In another aspect, the present invention further relates to a method for preparing a cured layer, comprising at least the following steps (i^a) and (i^b):

(i^a) providing the composition of the present invention onto a substrate, preferably by printing, preferably by spin-coating or ink-jetting;

(i^d) optionally bringing the composition into contact with a superstrate;

(i^b) curing the composition by heat and/or by irradiating the composition with light to form a cured layer;

(i^e) optionally removing the superstrate from the cured layer.

- [0019] In another aspect, the present invention also relates to a cured layer, preferably it is a photo-cured layer obtained or obtainable by the method of the present invention.
- [0020] In another aspect, the present invention also relates to a cured layer, preferably it is a photo-cured layer formed from the composition of the present invention.
- [0021] In another aspect, the present invention also relates to a stacked layer comprising a substrate and the cured layer of the present invention at least partly overlying the substrate.
- [0022] The present invention provides one or more of the following technical effects: improved thermal stability after curing, preferably at about 350°C or more; lower shrinkage after curing; improved etching resistance of a cured layer; improved planarization performance of a cured layer, namely over different pattern topographies of a substrate; lower viscosity and/or lower vapor pressure as a composition, preferably suitable for ink-jet printing.

Brief Description of Drawings

- [0023] [Fig.1]FIG. 1: Comparison of the isothermal baking behavior of Example 2 vs. a mixture of Example 2 (75wt%) and Example 7 (25wt%).
- [0024] [Fig.2]FIG. 2: Comparison of the isothermal baking behavior of Example 2 vs. a mixture of Example 2 (80wt%) and Example 5 (20wt%).
- [0025] [Fig.3]FIG. 3: Comparison of the isothermal baking behavior of Example 1 vs. a mixture of Example 1 (50wt%) and Example 2 (50wt%).
- [0026] [Fig.4]FIG. 4: Comparison of the isothermal baking behavior of Example 2 vs. a mixture of Example 2 (80wt%) and CAS: 2934745-89-6 (20wt%).
- [0027] [Fig.5]FIG. 5: Comparison of the isothermal baking behavior of Example 6 vs. a mixture of Example 6 (80wt%) and Example 12 (20wt%).

Description of Embodiments

- [0028] The terms as used herein have the following meanings:
The articles “a,” “an,” and “the” include plural referents unless otherwise expressly and unequivocally limited to one referent.
- [0029] Since all numbers, values and/or expressions referring to quantities of ingredients, reaction conditions, etc., used herein and in the claims appended hereto, are subject to the various uncertainties of measurement encountered in obtaining such values, unless otherwise indicated, all are to be understood as modified in all instances by the term “about.”
- [0030] Where a numerical range is disclosed herein such range is continuous, inclusive of both the minimum and maximum values of the range as well as every value between such minimum and maximum values. Still further, where a range refers to integers, every integer between the minimum and maximum values of such range is included. In

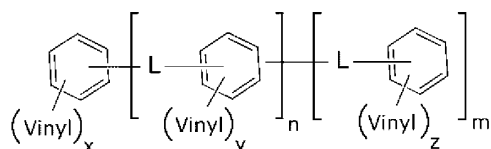
addition, where multiple ranges are provided to describe a feature or characteristic, such ranges can be combined. That is to say that, unless otherwise indicated, all ranges disclosed herein are to be understood to encompass any and all sub-ranges subsumed therein.

[0031] For example, a stated range of from “1 to 10” should be considered to include any and all sub-ranges between the minimum value of 1 and the maximum value of 10. Exemplary sub-ranges of the range 1 to 10 include, but are not limited to, 1 to 6.1, 3.5 to 7.8, and 5.5 to 10, etc.

[0032] The term “adhesion promoter” as used herein, refers to an additive that increases the adhesion of a given formulation.

[0033] The term “surfactant” as used herein, refers to an additive that reduces the adhesion force of the composition.

[0034] According to the present invention, said curable composition, preferably being a photo-curable composition, comprises at least a 1st monomer compound, a 2nd monomer compound and a polymerization initiator, wherein said 1st monomer compound is represented by chemical formula (I):



- (I)

wherein

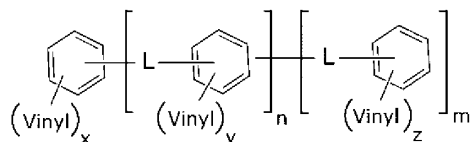
$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 ;

wherein said 2nd monomer compound is represented by chemical formula (I') and the 1st monomer compound and the 2nd monomer compound are different of each other.



(I')

wherein

$1 \leq x \leq 5, 0 \leq y \leq 4, 0 \leq z \leq 5;$

n is 1 or 0, m is 1 or 0;

$1 \leq n+m \leq 2$ or n+m can be 0 when x is $3 \leq x \leq 5;$

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 .

[0035] In a preferable embodiment of the present invention, said composition is a composition to be used for Inkjet Adaptive Planarization (IAP).

[0036] 1st monomer compound

According to the present invention, said 1st monomer compound represented by chemical formula (I) satisfies the condition of $1 \leq n+m \leq 2$. Preferably, n is 0 and m is 1.

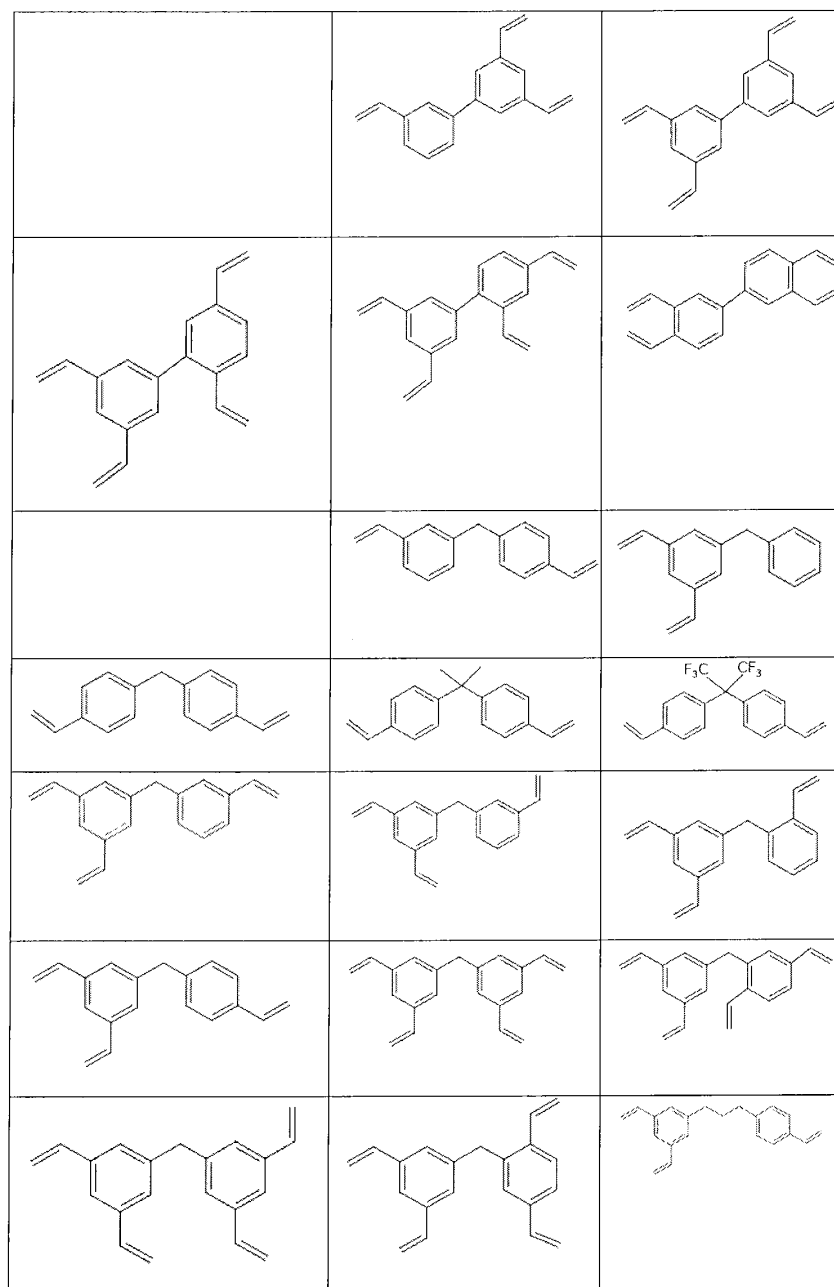
[0037] It is believed that compounds containing high carbon content, preferably 80% or more in said compound, are useful for realizing carbon-rich flat underlayer, and low viscosity with relatively low vapor pressure can be ideally used in inkjet printing process, namely in the Inkjet Adaptive Planarization (IAP) process according to the present invention. It is further believed that the 1st monomer compound is a vinylbenzene derivative which can form highly crosslinked thermosets after UV-induced radical polymerization. A high crosslinking density contributes to increasing chemical and thermal stability and is the key to its function as hard- mask.

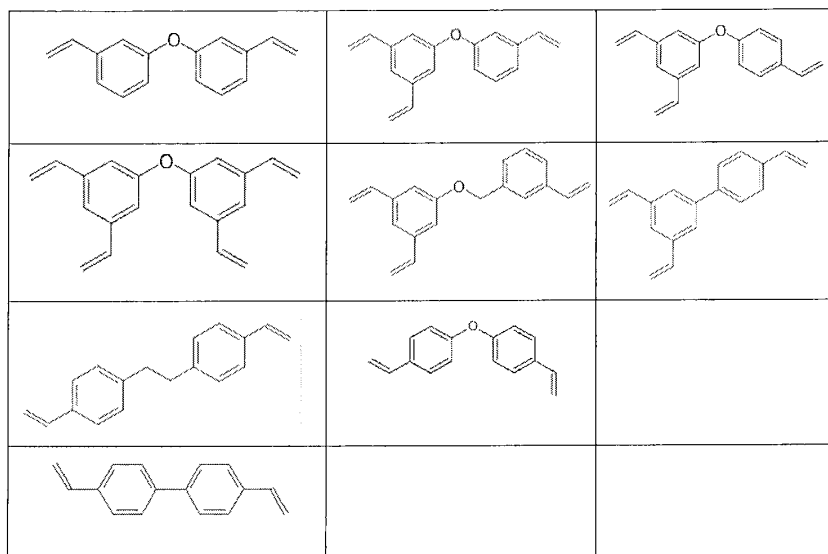
[0038] The 1st monomer having 4 or more vinyl groups may realize improved crosslinking property of the monomer.

[0039] Preferably, L of the chemical formula (I) is a direct bond, straight alkylene group having carbon atoms 1 to 5, straight alkenylene group having carbon atoms 2 to 5, wherein one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 .

[0040] Below table A shows preferable examples of the 1st monomer compound.

TableA:

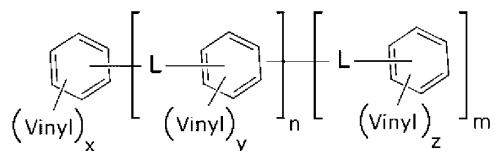




[0041] In a preferred embodiment of the present invention, the total amount of the 1st monomer compound is in the range from 10wt% to 99.9wt% based on the total amount of the composition, preferably it is from 50 to 99.9wt%, more preferably from 80 to 99wt%.

[0042] 2nd monomer compound

According to the present invention, said composition contains a 2nd monomer compound represented by chemical formula (I'), wherein the 1st monomer compound and the 2nd monomer compound are different of each other.



(I')

where

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

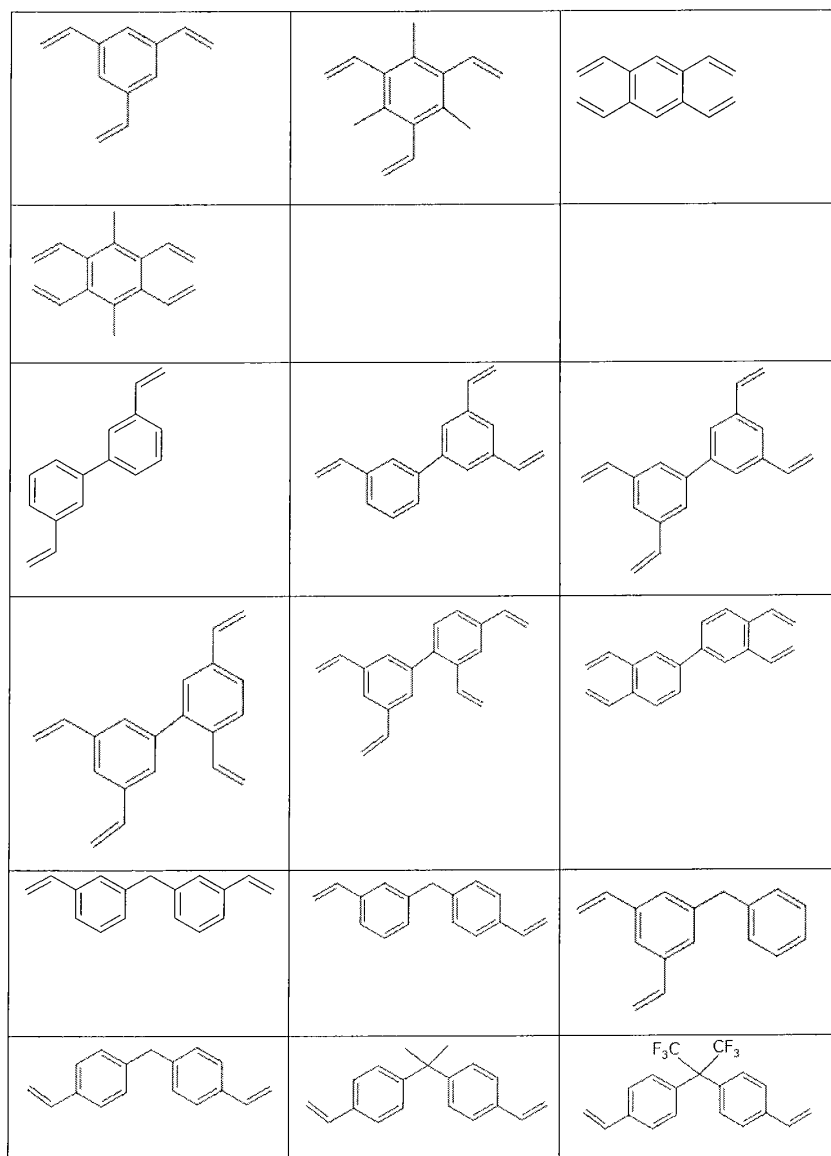
n is 1 or 0, m is 1 or 0;

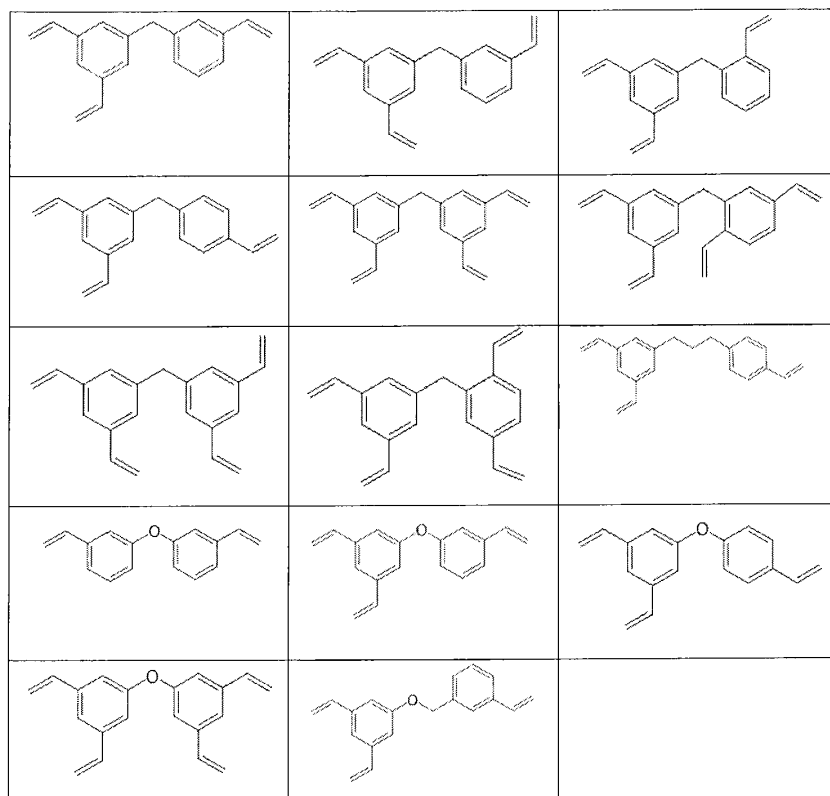
$1 \leq n+m \leq 2$ or $n+m$ can be 0 when x is $3 \leq x \leq 5$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 .

- [0043] As discussed in the 1st monomer compound above, it is believed that compounds containing high carbon content, preferably 80% or more in said compound, are useful for realizing carbon-rich flat underlayer, and low viscosity with relatively low vapor pressure can be ideally used in inkjet printing process, namely in the inkjet Adaptive Planarization (IAP) process according to the present invention. It is further believed that the 2nd monomer compound is a vinylbenzene derivative which can form highly crosslinked thermosets after UV-induced radical polymerization. A high crosslinking density contributes to increasing chemical and thermal stability and is the key to its function as hardmask.
- [0044] By adding the 2nd monomer compound in addition to the 1st monomer compound, and by controlling the mixing ratio, the viscosity, crosslinking property, vapor pressure of the composition and/or thermal stability, shrinkage after curing; improved etching resistance of a cured layer; improved planarization performance of a cured layer; can be controlled.
- [0045] In a preferred embodiment of the present invention, the total amount of the 1st monomer compound and the 2nd monomer compound is in the range from 10wt% to 99.9wt% based on the total amount of the composition. preferably it is from 50 to 99.9 wt%, more preferably from 80 to 99 wt%.
- [0046] Below Table B shows preferable examples of the 2nd monomer compound.
TableB:





[0047] 3rd/4th monomer compounds

In some embodiments of the present invention, the composition may optionally contain a 3rd and/or a 4th monomer compound. Said 3rd and/or 4th monomer compounds are different of each other and it also differ from the 1st and the 2nd monomer compounds. Said 3rd and/or 4th monomer compounds are represented by chemical formula (I'). Said 3rd and/or 4th monomer compounds can be selected from Table B.

[0048] Polymerization initiator

The polymerization initiator of the present invention includes a polymerization initiator that generates an acid, a base or a radical by radiation, and a polymerization initiator that generates an acid, a base or a radical by heat.

[0049] Preferably said polymerization initiator is selected from photo-radical initiators, photo-acid generators or a combination of photo-radical initiator and photo-acid generator. Examples are like Irgacure OXE02 (Boc Sciences, CAS: 478556-66-0), Omnirad 1316 (IGM Resins), Irgacure651 (Merck, CAS: 24650-42-8) and Irgacure819 (Merck, CAS: 162881-26-7).

[0050] According to the present invention, publicly available one like described in EP 3717966 A1 or WO 2021/099236 A1, can be used preferably.

[0051] Composition

In a preferred embodiment of the present invention, the composition comprises an acrylate monomer 10wt% or less based on the total amount of the composition, preferably it is in the range from 0 to 10wt%, more preferably it is in the range from 0 to 5wt%, more preferably it is an acrylate free composition comprising 0wt% of acrylate monomer.

[0052] It is believed that containing an acrylate monomer 10wt% or less leads significantly higher carbon content of a cured film obtained from the composition. Said higher carbon content leads improved etching resistance, which crucial for the function as carbon-rich hard mask and the pattern etch transfer. Furthermore, it is believed that acrylates reduce temperature stability of a cured film and leads higher degree of UV-induced shrinkage in photocurable systems. By reducing the total content of acrylate monomer in the composition 10wt% or less based on the total amount of the composition, more preferably it is in the range from 0 to 5wt%, such disadvantages of using acrylate can be reduced or resolved.

[0053] On the other hand, it is believed that adding small amount of acrylates may give flexibility on adjusting viscosity, inkjettability and/or vapor pressure of the composition. It can also increase photo curing speed of the composition.

[0054] Preferably, the composition of the present invention comprises a solvent 10wt% or less based on the total amount of the composition, preferably it is in the range from 0 to 10wt%, more preferably it is in the range from 0 to 5wt%, more preferably it is a solvent free composition comprises 0wt% of solvent.

[0055] It is believed that setting the total content of solvent(s) in the composition 10wt% or less based on the total amount of the composition is beneficial for reducing process steps, minimizing processing time, easy handling, namely for inkjetting, and/or minimizing/avoiding impurity contamination.

[0056] Additives

According to the present invention, in some embodiments, the composition may optionally comprises an additive selected from one or more members of the group consisting of surfactants, wetting agents, release agents, oxygen quenchers and stabilizers. In some embodiments, the amount of additives can be zero.

[0057] As said additive(s), publicly known materials preferably used in semiconducting industry can be used in the present invention.

[0058] It is believed that surfactants, release agents can be used to reduce adhesion force of the composition, preferably to the superstrate material for improved processability.

[0059] Viscosity

In a preferred embodiment of the present invention, the viscosity of the composition at 23°C is in the range from 5 to 50cP, preferably it is 5 to 20cP from the viewpoint of realizing smooth inkjetting.

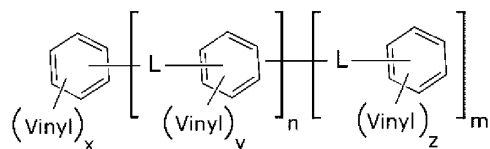
[0060] The viscosity of the composition can be controlled, for examples, by changing the type of the 1st monomer and/or the 2nd monomer, the amount of the 1st monomer and/or the 2nd monomer.

[0061] The viscosity of the composition of the present invention can be measured using an Anton Paar MCR 92 rheometer (Anton Paar, Granz, Austria) using a cone-plate geometry. Viscosity value is determined at a shear rate of 500s⁻¹ using a rotational cone-plate geometry (d=25mm) at 23°C.

[0062] Method for preparing the composition

In another aspect, the present invention relates to method for preparing the composition of the present invention, comprises at least the following step (A);

(A) Mixing at least a 1st monomer compound of formula (I), a 2nd monomer compound of formula (I') and a polymerization initiator



- (I)

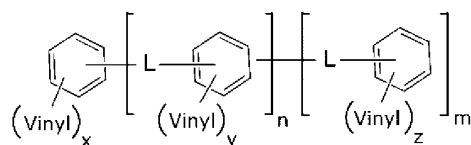
wherein

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 ;



(I')

wherein

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0;

$1 \leq n+m \leq 2$ or $n+m$ can be 0 when x is $3 \leq x \leq 5$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having

carbon atoms 2 to 15,

where one or more non-adjacent CH₂ groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂.

- [0063] In another aspect, the present invention further relates to method for preparing the cured layer, comprising at least the following steps (i^a) and (i^b):
- (i^a) providing the composition of the present invention onto a substrate, preferably by printing, preferably by spin-coating or ink-jetting;
 - (i^d) optionally bringing the composition into contact with a superstrate;
 - (i^b) curing the composition by heat and/or by irradiating the composition with light to form acured layer;
 - (i^e) optionally removing the superstrate from the cured layer.
- [0064] As for superstrate, publicly known one can be used. For example, the superstrate and it is method like described in Niyaz Khusnatdinov et. al., "Development of an inkjet-enabled Adaptive Planarization Process", Proceedings Volume 10451, Photomask Technology 2017; 104511A (2017), can be used preferably.
- [0065] In some embodiments, said curing can be a photo combination of photo curing, heatcuring or a combination of photo curing and heat curing.
- [0066] In a preferred embodiment, said photo curing is performed by irradiating the composition with UV light with curing energies in the range from 0.1 to 30 J/cm², more preferred is from 0.3 to 25J/cm². Further preferred one is from 0.5 to 2J/cm². Preferred UV light wavelength is 250nm to 400nm, more preferably around 350nm.
- [0067] In a preferred embodiment, said method further contains following step (i^c) after step (i^b):
- (i^c) baking the cured layer at the temperature in the range from 180 to 450°C, for the time in the range from 0.5 min to 10min.
- [0068] In a preferred embodiment, said method for preparing the cured layer is Inkjet Adaptive Planarization (IAP).
- [0069] In another aspect, the present invention further relates to a cured layer, preferably it is a photo-cured layer, obtained or obtainable by the method of the present invention.
- [0070] In another aspect, the present invention also relates to a cured layer, preferably it is a photo-cured layer, formed from the composition of the present invention. In a preferable embodiment, said photo-cured layer is a to be used as an interlayer insulating film of a semiconductor device or as an underlayer Spin-on carbon (SOC) for fabricating semiconductors. Such as LSI, system LSI, DRAM, SDRAM, RDRAM or D-RDRAM.
- [0071] In another aspect, the present invention further relates to a stacked layer comprising a substrate and the cured layer of the present invention at least partly overlying the

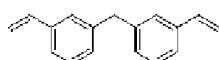
substrate.

[0072] The present invention is further illustrated by the examples following hereinafter which shall in no way be construed as limiting. The skilled person will acknowledge that various modifications, additions and alternations may be made to the invention without departing from the spirit and scope of the invention as defined in the appended claims.

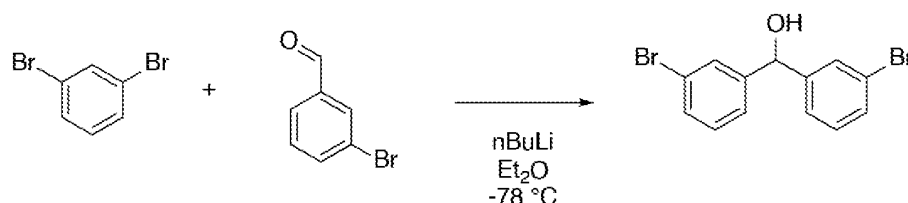
[0073] Examples

[0074] Part A: Synthesis of chemical compounds

[0075] Synthesis Example 1: Preparation of bis(3-vinylphenyl)methane

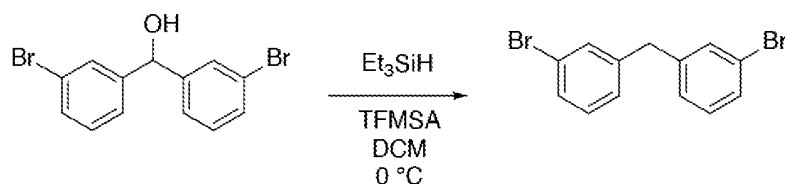


[0076] Step 1: Synthesis of bis(3-bromophenyl)methanol



1,3-Dibromobenzene (Merck, CAS: 108-36-1, 33.7 g, 143 mmol) is dissolved in anhydrous diethyl ether (Merck, 585 mL). The solution is cooled to -78°C and *n*-butyllithium solution (1.6 M in hexane, 98 mL, 156 mmol) is added dropwise. Then, 3-bromobenzaldehyde (Merck, CAS: 3132-99-8, 24 g, 130 mmol) is added and the reaction mixture stirred while it is brought to room temperature. The mixture is carefully quenched with 100 mL brine, separated and the aqueous phase extracted 3 times with DCM. The combined organic phases are dried over Na_2SO_4 , filtered and the solvent removed under vacuum, resulting 51.6 g (116 %) of a brown oil that is used without further purification.

[0077] Step 2: Synthesis of bis(3-bromophenyl)methane

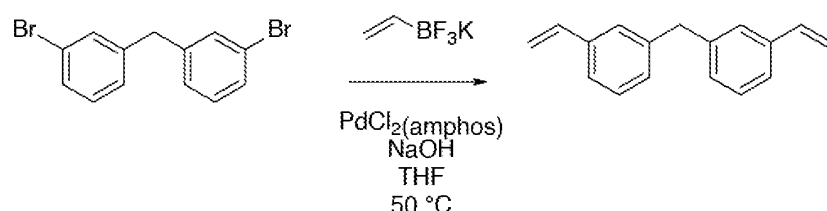


Bis(3-bromophenyl)methanol (51.6 g, 140 mmol) is dissolved in 400 mL DCM, treated with triethylsilane (Merck, CAS: 617-86-7, 88 mL, 550 mmol) and cooled to 0°C . Trifluoromethanesulfonic acid (Merck, CAS: 1493-13-6, 48 mL, 550 mmol) is added dropwise and the mixture stirred at room temperature for 3 h. Ice is carefully added and the aqueous phase is separated 3 times with DCM. The combined organic

phases are dried over Na_2SO_4 , filtered and the solvent removed under vacuum, resulting 110 g of a yellow oil. The product (35 g, 78%) is obtained by crystallization in ethanol.

[0078] ^1H NMR (500 MHz, Chloroform- d): δ = 7.38 (dt, J = 7.9, 1.4 Hz, 2H), 7.35 (d, J = 1.9 Hz, 2H), 7.19 (t, J = 7.7 Hz, 2H), 7.12 (d, J = 7.7 Hz, 2H), 3.93 (s, 2H) ppm.

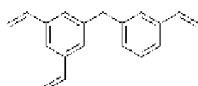
[0079] Step 3: Synthesis of bis(3-vinylphenyl)methane



Bis(3-bromophenyl)methanol (29 g, 90mmol) is dissolved in anhydrous THF (1.4 L), treated with potassium vinyltrifluoroborate (Merck, CAS:13682-77-4, 196 mmol, 26 g) and stirred under nitrogen at room temperature for 1 h. A NaOH solution (250 mL, 10wt%) and Pd(amphos) Cl_2 (Merck, CAS: 887919-35-9, 2.5 g, 3.6 mmol) is added and the reaction mixture stirred at 50 °C for 12 h. The mixture is cooled to room temperature, treated with water and extracted 3 times with ethyl acetate. The combined organic phases are dried over Na_2SO_4 , filtered and the solvent removed under vacuum. The crude product is purified with silica column chromatography using heptane as solvent, which eventually yielded 12.3 g (62.5 %) of a colorless liquid.

[0080] ^1H NMR (500 MHz, Chloroform- d): δ = 7.35 - 7.26 (m, 6H), 7.13 (dt, J = 6.7, 2.0 Hz, 2H), 6.74 (dd, J = 17.6, 10.9 Hz, 2H), 5.77 (d, J = 17.5 Hz, 2H), 5.27 (d, J = 10.9 Hz, 2H), 4.02 (s, 2H) ppm.

[0081] Synthesis Example 2: Preparation of 1,3-divinyl-5-(3-vinylbenzyl)benzene

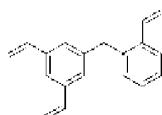


[0082] In general, the same synthesis conditions are used as for Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene.

[0083] 18.5 g (78%) of a colorless liquid is obtained in the Suzuki step.

[0084] ^1H NMR (500 MHz, Chloroform- d) δ = 7.35 (d, J = 1.8 Hz, 1H), 7.34 - 7.26 (m, 3H), 7.18 (d, J = 1.5 Hz, 2H), 7.13 (dt, J = 6.9, 1.9 Hz, 1H), 6.73 (ddd, J = 17.6, 10.8, 3.7 Hz, 3H), 5.78 (ddd, J = 17.6, 4.4, 0.9 Hz, 3H), 5.28 (ddd, J = 10.9, 5.6, 1.0 Hz, 3H), 4.01 (s, 2H) ppm.

[0085] Synthesis Example 3: Preparation of 1,3-divinyl-5-(2-vinylbenzyl)benzene

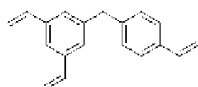


[0086] In general, the same synthesis conditions are used as for Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 2-bromobenzaldehyde (Merck, CAS: 6630-33-7) instead of 3-bromobenzaldehyde.

[0087] 4.4 g (90%) of a colorless liquid is obtained in the Suzuki step.

[0088] ¹HNMR (500 MHz, Chloroform-d) δ = 7.57 (dd, J = 7.1, 2.1 Hz, 1H), 7.35 - 7.19 (m, 3H), 7.16 (dd, J = 7.0, 2.0 Hz, 1H), 7.10 (d, J = 1.5 Hz, 2H), 6.99 (dd, J = 17.3, 11.0 Hz, 1H), 6.70 (dd, J = 17.6, 10.8 Hz, 2H), 5.76 (d, J = 1.0 Hz, 1H), 5.72 (d, J = 1.0 Hz, 1H), 5.68 (dd, J = 17.3, 1.4 Hz, 1H), 5.30 (dd, J = 11.0, 1.4 Hz, 1H), 5.26 (dd, J = 10.8, 0.9 Hz, 2H), 4.09 (s, 2H) ppm.

[0089] Synthesis Example 4: Preparation of 1,3-divinyl-5-(4-vinylbenzyl)benzene

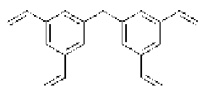


[0090] In general, the same synthesis conditions are used as for Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 4-bromobenzaldehyde (Merck, CAS: 1122-91-4) instead of 3-bromobenzaldehyde.

[0091] 17.5 g (97%) of a colorless liquid is obtained in the Suzuki step.

[0092] ¹HNMR (500 MHz, Chloroform-d) δ = 7.42 - 7.38 (m, 2H), 7.36 (s, 1H), 7.24 - 7.17 (m, 4H), 6.75 (d, J = 17.6, 10.9, 8.1 Hz, 3H), 5.81 (s, 1H), 5.82 - 5.73 (m, 2H), 5.31 (s, 1H), 5.30 - 5.24 (m, 2H), 4.01 (s, 2H) ppm.

[0093] Synthesis Example 5: Preparation of bis(3,5-divinylphenyl)methane

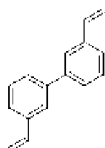


[0094] In general, the same synthesis conditions are used as for Example 1. In step 1, 1,3,5-tribromobenzene (Merck, CAS: 626-39-1) is used instead of 1,3-dibromobenzene and 3,5-dibromobenzaldehyde (Merck, CAS: 56990-02-4) instead of 3-bromobenzaldehyde.

[0095] 4.5 g (63%) of a colorless solid is obtained in the Suzuki step.

[0096] ¹HNMR (500 MHz, Chloroform-d) δ = 7.34 (d, J = 1.7 Hz, 2H), 7.17 (d, J = 1.6 Hz, 4H), 6.71 (dd, J = 17.6, 10.8 Hz, 4H), 5.77 (dd, J = 17.7, 0.9 Hz, 4H), 5.27 (dd, J = 10.8, 0.9 Hz, 4H), 3.99 (s, 2H) ppm.

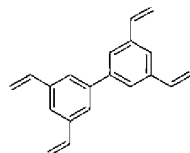
[0097] Synthesis Example 6: Preparation of 3,3'-divinyl-1,1'-biphenyl



[0098] Example 6 is synthesized using 3,3'-dibromo-1,1'-biphenyl (abcr, CAS: 16400-51-4) with the same conditions as step 3 of Example 1.

[0099] ^1H NMR (500 MHz, Chloroform- d) δ = 7.68 (q, J = 1.5 Hz, 2H), 7.55 (dt, J = 6.2, 2.2 Hz, 2H), 7.51 - 7.44 (m, 4H), 6.85 (dd, J = 17.6, 10.9 Hz, 2H), 5.89 (dd, J = 17.6, 0.9 Hz, 2H), 5.36 (dd, J = 10.9, 0.9 Hz, 2H) ppm.

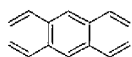
[0100] Synthesis Example 7: Preparation of 3,3',5,5'-tetravinyl-1,1'-biphenyl



[0101] Example 7 is synthesized using 3,3',5,5'-tetrabromobiphenyl (abcr, CAS: 16400-50-3) with the same conditions as step 3 of Example 1.

[0102] ^1H NMR (500 MHz, THF- d_8) δ = 7.65 (d, J = 1.5 Hz, 4H), 7.55 (t, J = 1.7 Hz, 2H), 6.85 (dd, J = 17.6, 10.9 Hz, 4H), 5.93 (dd, J = 17.6, 0.9 Hz, 4H), 5.31 (dd, J = 10.8, 0.9 Hz, 4H) ppm.

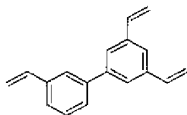
[0103] Synthesis Example 8: Preparation of 1,2,4,5-tetravinylbenzene



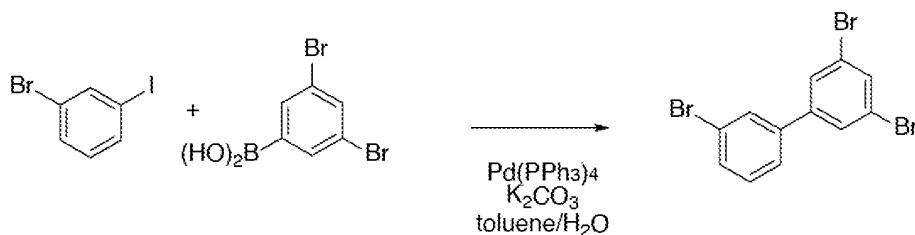
[0104] Example 8 is synthesized using 1,2,4,5-tetrabromobenzene (Merck, CAS: 636-28-2) with the same conditions as step 3 of Example 1.

[0105] ^1H NMR (500 MHz, Methylene Chloride- d_2) δ = 7.54 (s, 2H), 6.98 (dd, J = 17.4, 11.0 Hz, 4H), 5.66 (dd, J = 17.4, 1.3 Hz, 4H), 5.32 (dd, J = 11.0, 1.3 Hz, 4H) ppm.

[0106] Synthesis Example 9: Preparation of 3,3',5-trivinyl-1,1'-biphenyl



[0107] Step 1: Synthesis of 3,3',5-tribromo-1,1'-biphenyl



3-Bromo-1-iodobenzene (Merck, CAS:591-18-4, 20 g, 70.7 mmol) is dissolved together with 3,5-dibromophenylboronic acid (Merck, CAS: 117695-55-3, 19.8 g, 70.7 mmol) in toluene (325 mL) and water (300 mL). K_2CO_3 (48.9 g, 353 mmol) and tetrakis(triphenylphosphine)palladium (Merck, 0.41 g, 0.35 mmol) are added and the mixture stirred overnight at reflux under nitrogen. The mixture is cooled to room tem-

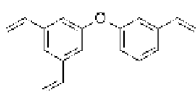
perature and the phases separated. The aqueous phase is extracted 3 times with ethyl acetate, the organic phases are combined and dried over Na_2SO_4 , filtered and evaporated to dryness. The crude product is purified by silica chromatography using heptane as eluent, yielding 18.5 (67 %) of a colorless solid.

[0108] Step 2: Synthesis of 3,3',5-trivinyl-1,1'-biphenyl

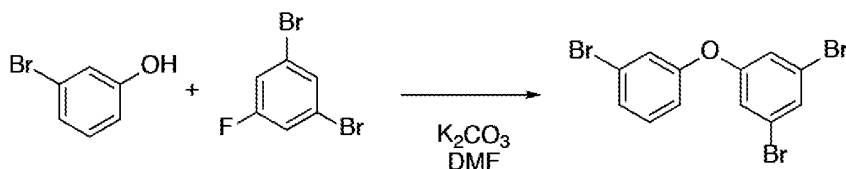
[0109] Example 9 is synthesized using 3,3',5-tribromo-1,1'-biphenyl (step 1) with the same conditions as step 3 of Example 1.

[0110] ^1H NMR (500 MHz, Chloroform- d) δ = 7.68 (d, J = 1.9 Hz, 1H), 7.60 - 7.50 (m, 3H), 7.52 - 7.43 (m, 3H), 6.85 (ddd, J = 17.6, 10.9, 4.3 Hz, 3H), 5.94 - 5.85 (m, 3H), 5.37 (dd, J = 11.0, 4.6 Hz, 3H) ppm.

[0111] Synthesis Example 10: Preparation of 1,3-divinyl-5-(3-vinylphenoxy) benzene



[0112] Step 1: Synthesis of 1,3-dibromo-5-(3-bromophenoxy)benzene



3-Bromophenol (Merck, CAS: 591-20-8, 6.8 g, 39.4 mmol) is dissolved together with 1,3-dibromo-5-fluorobenzene (Merck, CAS: 1435-51-4, 10 g, 39.4 mmol) and K_2CO_3 (5.4 g, 39.4 mmol) in DMF (91.5 mL) and treated overnight at 160 °C under nitrogen. The reaction mixture is cooled to room temperature and treated with water, forming an oil. The aqueous phase is extracted twice with MTBE and the combined organic phases are dried with Na_2SO_4 , filtered and evaporated to dryness. Finally, the crude product is purified by silica chromatography (heptane/ethyl acetate, 9 : 1), wherein 13 g (81 %) of a colorless solid are obtained.

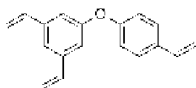
[0113] ^1H NMR (500 MHz, Chloroform- d) δ = 7.45 (t, J = 1.6 Hz, 1H), 7.35 (ddd, J = 7.9, 1.8, 1.0 Hz, 1H), 7.27 (t, J = 8.1 Hz, 1H), 7.21 (t, J = 2.1 Hz, 1H), 7.10 (d, J = 1.6 Hz, 2H), 6.98 (ddd, J = 8.2, 2.4, 1.0 Hz, 1H) ppm.

[0114] Step 2: Synthesis of 1,3-divinyl-5-(3-vinylphenoxy)benzene

[0115] Example 10 is synthesized using 1,3-dibromo-5-(3-bromophenoxy)benzene (step 1) with the same conditions as step 3 of Example 1.

[0116] ^1H NMR (500 MHz, Chloroform- d) δ = 7.33 (t, J = 7.9 Hz, 1H), 7.25 - 7.17 (m, 2H), 7.13 (t, J = 2.1 Hz, 1H), 7.02 (d, J = 1.4 Hz, 2H), 6.95 (dd, J = 8.1, 2.4 Hz, 1H), 6.71 (ddd, J = 17.6, 10.8, 6.7 Hz, 3H), 5.77 (d, J = 17.6 Hz, 3H), 5.31 (dd, J = 10.8, 3.1 Hz, 3H) ppm.

[0117] Synthesis Example 11: Preparation of 1,3-divinyl-5-(4-vinylphenoxy) benzene



[0118] Step 1: Synthesis of 1,3-dibromo-5-(4-bromophenoxy)benzene

[0119] The synthesis is carried out according to step 1 of Example 10, wherein 3-bromophenol is replaced by 4-bromophenol (Merck, CAS:106-41-2). 11 g (69 %) of a colorless solid is obtained.

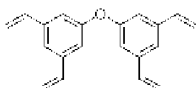
[0120] ¹HNMR (500 MHz, THF-d₈) δ = 7.55 - 7.50 (m, 2H), 7.48 (t, J = 1.7 Hz, 1H), 7.16 (d, J = 1.7 Hz, 2H), 7.03 - 6.95 (m, 2H) ppm.

[0121] Step 2: Synthesis of 1,3-divinyl-5-(4-vinylphenoxy)benzene

[0122] Example 11 is synthesized using 1,3-dibromo-5-(4-bromophenoxy)benzene (step 1) with the same conditions as step 3 of Example 1.

[0123] ¹HNMR (500 MHz, THF-d₈) δ = 7.42 - 7.36 (m, 2H), 7.25 (t, J = 1.6 Hz, 1H), 7.02 (d, J = 1.6 Hz, 2H), 6.99 - 6.93 (m, 2H), 6.68 (ddd, J = 17.6, 10.9, 3.0 Hz, 3H), 5.76 (dd, J = 17.6, 1.0 Hz, 2H), 5.67 (dd, J = 17.6, 1.0 Hz, 1H), 5.22 (dd, J = 11.0, 1.0 Hz, 2H), 5.14 (dd, J = 11.0, 1.0 Hz, 1H) ppm.

[0124] Synthesis Example 12: Preparation of 5,5'-oxybis(1,3-divinylbenzene)



[0125] Step 1: Synthesis of 5,5'-oxybis(1,3-dibromobenzene)

[0126] The synthesis is carried out according to step 1 of Example 10, 3-bromophenol is replaced by 3,5-dibromophenol (Merck, CAS: 626-41-5). 6.8 g (69 %) of a colorless solid is obtained.

[0127] ¹HNMR (500 MHz, CDCl₃) δ = 7.50 (t, J = 1.7 Hz, 2H), 7.12 (d, J = 1.6 Hz, 4H) ppm.

[0128] Step 2: Synthesis of 5,5'-oxybis(1,3-divinylbenzene)

[0129] Example 12 is synthesized using 5,5'-oxybis(1,3-dibromobenzene) (step 1) with the same conditions as step 3 of Example 1. 3.3 g (89 %) of a pale yellow liquid was obtained.

[0130] ¹HNMR (500 MHz, CDCl₃) δ = 7.23 (d, J = 1.6 Hz, 2H), 7.01 (d, J = 1.5 Hz, 4H), 6.70 (dd, J = 17.6, 10.9 Hz, 4H), 5.77 (dd, J = 17.5, 0.8 Hz, 4H), 5.35 - 5.23 (m 4H) ppm.

[0131] Part B: Preparing of photocurable compositions

[0132] Working Examples 13 to 25: preparation of photocurable compositions

[0133] The photocurable compositions (W.E.13 to W.E. 25) contain at least one polyvinylbenzene compound, and are formulated based on the ratios presented in Table 2. Additionally, W.E. 14 & W.E. 25 include a poly-functional acrylate monomer (SR295, CAS:4986-89-4), while W.E. 23 features a mixed vinyl-acrylate compound

(CAS:2934745-89-6) as prior-art material. All compositions also contain a certain amount of a photoinitiator, the details of which will be specified below Table 2.

[0134] Viscosities

The viscosities of the photocurable compositions are measured using an Anton Paar MCR 92 rheometer (Anton Paar, Graz, Austria) using a cone-plate geometry. Viscosities are determined at a shear rate of 500 s^{-1} using a rotational cone-plate geometry ($d = 25 \text{ mm}$) at $23 \text{ }^{\circ}\text{C}$.

[0135] Thermal Stability of Photo-Cured Layers

Photo-cured films are prepared by applying a $60 \text{ }\mu\text{m}$ thick layer of the photocurable composition in a sandwich set-up consisting of two glass slides and curing the film at room temperature with UV light with a wavelength of 365 nm in varying curing energies (5.5 J/cm^2 or 10 J/cm^2). The films have been baked after UV-curing at $250 \text{ }^{\circ}\text{C}$ for 2 min on a hotplate and then measured via TGA (TA Discovery or TA TGA Q50). The thermal stability of a composition can be assessed using either the 2% decomposition temperature ($T_{d2\%}$), the weight loss percentage per minute, or both. $T_{d2\%}$ is determined heating the cured polymer at a controlled rate of 10K/min . Weight loss percentage per minute is measured with an isothermal baking test by heating the sample to a pre-determined temperature ($400 \text{ }^{\circ}\text{C}$) in 20 minutes and holding the temperature constant for 60 minutes .

[0136] Table 1 shows an overview of a non-limiting number of different compositions based on just one vinylbenzene component together with either a) $3\text{wt}\%$ Irgacure OXE02 (BocSciences, CAS: 478556-66-0) & $3\text{wt}\%$ Irgacure651 (Merck, CAS: 24650-42-8) or b) $3\text{wt}\%$ Irgacure OXE02 & $3\text{wt}\%$ Irgacure819 (Merck, CAS: 162881-26-7) or c) $6\text{wt}\%$ Irgacure OXE02. Curing energy is 5.5 J/cm^2 or 10 J/cm^2 at 365 nm . After exposure the samples are baked for 2 minutes at $250 \text{ }^{\circ}\text{C}$ on a hotplate.

[0137] For examples, Example 1^a in Table 1 means that the chemical compound from synthesis example 1 is used together with a) $3\text{wt}\%$ Irgacure OXE02 & $3\text{wt}\%$ Irgacure 651.

[0138] Example 6^b in Table 1 means that the chemical compound from synthesis example 6 is used together with b) $3\text{wt}\%$ Irgacure OXE02 & $3\text{wt}\%$ Irgacure 819.

[0139] And Example 10^c in Table 1 means that the chemical compound from synthesis example 10 is used together with $6\text{wt}\%$ Irgacure OXE02.

[0140] Table 2 summarizes examples in which different ratios of different polyvinyl compounds and either a) $3\text{wt}\%$ Irgacure OXE02 & $3\text{wt}\%$ Irgacure651 or b) $3\text{wt}\%$ Irgacure OXE02 & $3\text{wt}\%$ Irgacure 819 or c) $6\text{wt}\%$ Irgacure OXE02 or d) $2\text{wt}\%$ Omnirad1316 (IGM Resins, CAS: 2417522-91-7) are used. Curing energy is 5.5J/cm^2 or 10J/cm^2 at 365 nm . After exposure the samples are baked for 2 minutes at $250 \text{ }^{\circ}\text{C}$ on a hotplate.

[0141] Table1:

Example	C-content	η^{23}	$T_{g2\%}$	weight
				loss/min at 400 °C
1 ^a	91.7 %	8.8 cP	-	0.91%/min
2 ^a	91.7 %	22.0 cP	435 °C	0.12 %/min
2 ^d	91.7 %	22.0 cP	-	0.17 %/min
3 ^a	91.7 %	23.9 cP	-	0.75%/min
4 ^a	91.7 %	22.4 cP	-	0.06%/min
6 ^b	92.1 %	23.0 cP	446 °C	0.87%/min
10 ^c	86.4 %	16.0 cP	426 °C	-
11 ^c	86.4 %	37.0 cP	478 °C	0.03%/min

3wt% Irgacure OXE02 & 3wt% Irgacure651

^b 3wt% Irgacure OXE02 & 3wt% Irgacure 819

^c 6wt% Irgacure OXE02

[0142] Table2:

Working Example	Cmpd 1	Cmpd 2	Cmpd 3	η^{23}	$T_{42\%}$	Weight
						loss%/min at 400 °C
W.E. 13 ^d	47.2 wt%	47.2 wt%	-	9.7 cP	432 °C	-
	Ex 6	Ex 8				
W.E. 14 ^d	47.2 wt%	37.7 wt%	9.4 wt%	11.0 cP	395 °C	-
	Ex 6	Ex 8	SR295			
W.E. 15 ^d	47.2 wt%	18.9 wt%	28.3 wt%	28.0 cP	460 °C	-
	Ex 6	Ex 8	Ex 7			
W.E. 16 ^d	56.6 wt%	37.7 wt%	-	47.0 cP	461 °C	-
	Ex 6	Ex 9				
W.E. 17 ^d	56.6 wt%	37.7 wt%	-	18.4 cP	435 °C	0.53%/min
	Ex 6	Ex 10				
W.E. 18 ^d	56.6 wt%	37.7 wt%	-	24.3 cP	450 °C	0.55%/min
	Ex 6	Ex 2				
W.E. 19 ^d	47.2wt%	47.2wt%	-	24.9 cP	450 °C	0.06%/min
	Ex 10	Ex 11				
W.E. 20 ^a	70.8wt%	23.6wt%	-	28.9 cP	-	0.04%/min
	Ex 2	Ex 7				
W.E. 21 ^a	75.5wt%	18.9wt%	-	33.2 cP	-	0.04%/min
	Ex 2	Ex 5				

W.E. 22 ^b	47.2wt% Ex 1	47.2wt% Ex 2	-	13.8 cP	-	0.48%/min
W.E. 23 ^c	75.5wt% Ex 2	18.9wt% 2934745- 89-6	-	17.8 cP	-	0.25%/min
W.E. 24 ^e	75.5wt% Ex 6	18.9wt% Ex 12	-	33.4 cP	451 °C	0.44%/min
W.E. 25 ^e	75.5wt% Ex 6	18.9wt% SR295	-	60.2 cP	433 °C-	0.97%/min

^a3wt% Irgacure OXE02 & 3wt% Irgacure 651 (5.5 J/cm² + 250 °C/2min)

^b3wt% Irgacure OXE02 & 3wt% Irgacure 651 (10 J/cm² + 250 °C/2min)

^c3wt% Irgacure OXE02 & 3wt% Irgacure 819 (10 J/cm² + 250 °C/2min)

^d6wt% Irgacure OXE02 (10 J/cm² + 250 °C/2min)

^e2wt% Omnirad 1316 & 4wt% Irgacure 651 (10 J/cm² - 250 °C/2min)

[0143] Part C: Relative etch resistance to benchmark acrylate-based photocurable composition.

[0144] Printed compositions of the present invention were etched using a reactive ion etching setup with O₂, CF₄ and Cl₂ plasma. The etch resistance was compared relative to a benchmark acrylate-based photocurable composition (CE1). CE1 was composed of 50 parts of Benzyl Acrylate, 30 parts of 1-Naphthyl Acrylate, and 20 parts of Bisphenol A dimethacrylate, with 3 parts of Irgacure 819 as photoinitiator. (see Table 3).

[0145] Photo-cured film layers Ex6, WE25 and CE1 were formed on a silicon wafer using a J-FIL Imprint Tool I450. The film layers were fully cured under UV exposure for 20J/cm² for Ex6 and WE25 or 2.4J/cm² for CE1. The thickness of the film layer after curing was about 80 to 100 nm. For measuring the etch resistance, dry etching was conducted using a Trion Oracle 3-Chamber Cluster System as etch tool. Three different dry etch chemistries were tested: 1) etching with an oxygen / argon gas combination (O₂/Ar) 2) etching with CF₄/Ar gas combination; and 3) etching with a combination of chlorine gas and oxygen (Cl₂/O₂) under the following conditions:

[0146]

Etch Conditions			
	O2/Ar etch	CF4/Ar etch	Cl2/O2 etch
O2 flow (sccm)	2	5	54
Argon Flow (sccm)	10	30	9
ICP Power (watts)	0	150	0
RIE Power (watts)	45	75	90
Pressure (mtorr)	10	120	150
ET (sec)	60	60	90
He BP (Torr)	5		
Chuck T (deg C)	8	8	8

[0147] Table3:

Example	C-content	O ₂ Etch	CF ₄ Etch	Cl ₂ Etch
		Rate	Rate	Rate
		(relative)	(relative)	(relative)
Ex 6 ^a	92.1 %	0.74	0.73	0.48
W.E. 25 ^b	91.8 %	0.62	0.58	0.29
CE1	75.8 %	1	1	1

^a+3wt% Irgacure OXE02 & 3wt% Irgacure 651

^bW.E. 25: Ex6 (60wt%), Ex8 (40 wt%), 3wt% Irgacure OXE02, 3wt% Irgacure 651

[0148] Part D: Nanoindentation test

[0149] Mechanical properties of printed compositions of the present invention were evaluated by nanoindentation. Nanoindentation methods were performed on photo-cured film layers of Ex6, WE25, WE26 and CE1 to measure reduced modulus and hardness. Tests were done with a Hysitron TI 950 Triboindenter using an Oliver-Pharr method integrated into TriboScan control software. In brief, 3 2 μ l drops of each sample were applied onto a Si wafer coated with adhesion layer coated and then covered with a quartz slides. A UV exposure of 20J/cm² (for WE25 and WE26) or 2.4J/cm² (for CE1) was used to cure the materials. The obtained Si wafer with cured film layers were then placed onto the stage of the Triboindenter within 72 hours of curing. A diamond indenter (90degree cube corner tip) was used to perform the indentations, which (shape) was calibrated by a standard fused silica. The reduced modulus E_r (GPa) was determined by measuring the load P and the displacement h (Contact depth, in nm). Hardness H (GPa) was found by dividing the load by the area of contact. Both E_r and H values were generated by the integrated software. An indented depth of 200 nm with a 5X5 array of points were used to average the E_r . The thickness of the cured layer films was 3 μ m or more to eliminate the effect of the substrates. The results are tabulated in Table 4.

[0150] Table 4

Example	Contact Depth [nm]		Modulus [GPa]		Hardness [GPa]	
	Avg	StDev	Avg	StDev	Avg	StDev
CE1	186.6	1.4	4.32	0.14	0.27	0.007
W.E. 25 ^a	167.2	1.1	5.90	0.13	0.79	0.023
W.E. 26 ^b	158.8	1.0	6.13	0.14	1.05	0.025
Ex 6 ^c	170.6	1.1	5.86	0.20	0.69	0.012

^aW.E.25: Ex6 (60wt%), Ex8 (40 wt%), 3wt% Irgacure OXE02, 3wt% Irgacure 651

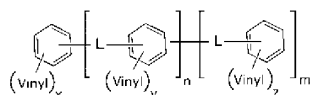
^bW.E.26: Ex6 (50wt%), Ex7 (50 wt%), 3wt% Irgacure OXE02, 3wt% Irgacure 651

^c+3wt% Irgacure OXE02 & 3wt% Irgacure 651

Claims

[Claim 1]

A curable composition, preferably being a photo-curable composition, comprising at least a 1st monomer compound, a 2nd monomer compound, and a polymerization initiator, wherein said 1st monomer compound is represented by chemical formula (I)



- (I)

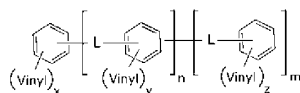
wherein

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15, where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 ;

wherein said 2nd monomer compound is represented by chemical formula (I'), and the 1st monomer compound and the 2nd monomer compound are different of each other.



(I')

where

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

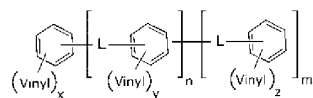
n is 1 or 0, m is 1 or 0;

$1 \leq n+m \leq 2$ or $n+m$ can be 0 when x is $3 \leq x \leq 5$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15, where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 .

- [Claim 2] The composition of claim 1, wherein n is 0 and m is 1.
- [Claim 3] The composition of claim 1 or 2, wherein L is a direct bond, straight alkylene group having carbon atoms 1 to 5, straight alkenylene group having carbon atoms 2 to 5, wherein one or more non-adjacent CH₂ groups of said alkylene or alkenylene group may be replaced by oxygen atom, C=O, C=S, C=Se, C=NH, SiH₂, SO, SO₂, OS, or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO₂.
- [Claim 4] The composition of any one of preceding claims, wherein the total amount of the 1st monomer compound is in the range from 10wt% to 99.9wt% based on the total amount of the composition, preferably it is from 50 to 99.9wt%, more preferably from 80 to 99wt%.
- [Claim 5] The composition of any one of preceding claims, wherein the total amount of the 1st monomer compound and the 2nd monomer compound is in the range from 10wt% to 99.9wt% based on the total amount of the composition. Preferably it is from 50 to 99.9wt%, more preferably from 80 to 99wt%.
- [Claim 6] The composition of any one of preceding claims, comprises an acrylate monomer 10wt% or less based on the total amount of the composition, preferably it is in the range from 0 to 10wt%, more preferably it is in the range from 0 to 5wt%, more preferably it is an acrylate free composition comprises 0wt% of acrylate monomer.
- [Claim 7] The composition of any one of preceding claims, comprises a solvent 10wt% or less based on the total amount of the composition, preferably it is in the range from 0 to 10wt%, more preferably it is in the range from 0 to 5wt%, more preferably it is a solvent free composition comprises 0wt% of solvent.
- [Claim 8] The composition of any one of preceding claims, comprises an additive selected from one or more members of the group consisting of surfactants, wetting agents, release agents, oxygen quenchers and stabilizers.
- [Claim 9] The composition of any of preceding claims, wherein the viscosity at 23°C is in the range from 5 to 50cP.
- [Claim 10] Method for preparing a composition of any one of claims 1 to 9, comprises at least the following step(A);
(A) Mixing at least a 1st monomer compound, of chemical formula (I), a 2nd monomer of chemical formula (I') and a polymerization initiator, wherein said 1st monomer compound and the 2nd monomer compound

are different of each other.



- (I)

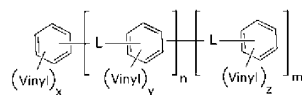
wherein

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0, $1 \leq n+m \leq 2$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 ;



(I')

wherein

$1 \leq x \leq 5$, $0 \leq y \leq 4$, $0 \leq z \leq 5$;

n is 1 or 0, m is 1 or 0;

$1 \leq n+m \leq 2$ or $n+m$ can be 0 when x is $3 \leq x \leq 5$;

L is at each occurrence, same or differently selected from the group consisting of a direct bond, alkylene group having carbon atoms 1 to 15, and alkenylene group having carbon atoms 2 to 15,

where one or more non-adjacent CH_2 groups of said alkylene or alkenylene group may be replaced by oxygen atom, $\text{C}=\text{O}$, $\text{C}=\text{S}$, $\text{C}=\text{Se}$, $\text{C}=\text{NH}$, SiH_2 , SO , SO_2 , OS , or CONH and where one or more H atoms may be replaced by D, F, Cl, Br, I, CN or NO_2 .

[Claim 11]

Method for preparing a cured layer, comprising at least the following steps (i^a) and (i^b):

(i^a) providing the composition of any one of claims 1 to 9 onto a substrate, preferably by printing, preferably by spin-coating or ink-jetting;

(i^d) optionally bringing the composition into contact with a superstrate;

(i^b) curing the composition by heat and/or by irradiating the composition with light to form a cured layer;

- (i^c) optionally removing the superstrate from the cured layer.
- [Claim 12] Method of claim 11, further contains following step (i^c) after step (i^b);
(i^c) baking the cured layer at the temperature in the range from 180 to 450°C, for the time in the range from 0.5min to 10min.
- [Claim 13] A cured layer, preferably it is a photo-cured layer obtained or obtainable by the method of claim 11 or 12.
- [Claim 14] A cured layer, preferably it is a photo-cured layer formed from the composition of any one of claims 1 to 9.
- [Claim 15] A stacked layer comprising a substrate and the cured layer of claim 13 or 14 at least partly overlying the substrate.