(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau

(43) International Publication Date
19 December 2024 (19.12.2024)

WIPO | PCT

(10) International Publication Number
WO 2024/258344 A1

(51) International Patent Classification:
G03F 7/00 (2006.01) *C08L 33/16* (2006.01)
G03F 7/004 (2006.01) *C08K 3/22* (2006.01)
C08L 33/12 (2006.01)

(21) International Application Number:
PCT/SG2024/050353

(22) International Filing Date:
27 May 2024 (27.05.2024)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
10202301701R 15 June 2023 (15.06.2023) SG

(71) Applicants: **AGENCY FOR SCIENCE, TECHNOLOGY AND RESEARCH** [SG/SG]; 1 Fusionopolis Way, #20-10, Connexis North, Singapore 138632 (SG). **NATIONAL UNIVERSITY OF SINGAPORE** [SG/SG]; 21 Lower Kent Ridge Road, Singapore 119077 (SG).

(72) Inventors: **MIN, Jiakang**; c/o Department of Materials Science & Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575 (SG). **LIU, Siqi**; c/o Department of Materials Science & Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575 (SG). **HE, Chaobin**; c/o Department of Materials Science & Engineering, National University of Singapore, 9 Engineering Drive 1, Singapore 117575 (SG). **LIU, Hong**; c/o Institute of Materials Research and Engineering, 2 Fusionopolis Way, #08-03, Innovis, Singapore 138634 (SG). **SURESH, Vignesh**; c/o Institute of Materials Research and Engineering, 2 Fusionopolis Way, #08-03, Innovis, Singapore 138634 (SG).

(74) Agent: **CSASIA IP PTE. LTD.**; 47 Scotts Road, #13-03, Goldbell Towers, Singapore 228233 (SG).

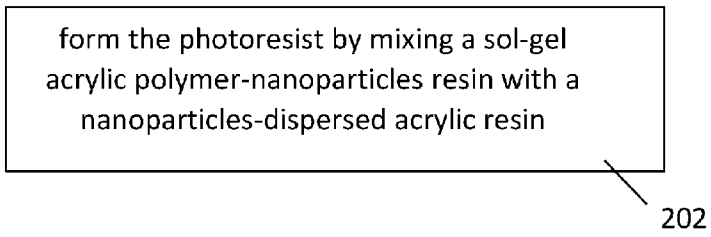
(81) Designated States *(unless otherwise indicated, for every kind of national protection available)*: AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CV, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IQ, IR, IS, IT, JM, JO, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, MG, MK, MN, MU, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, WS, ZA, ZM, ZW.

(84) Designated States *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, CV, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SC, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, ME, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

Published:
— *with international search report (Art. 21(3))*

(54) Title: PHOTORESIST AND METHOD OF FORMING THE SAME, NANOIMPRINTING METHOD

FIG. 2



(57) Abstract: Various embodiments may relate to a method of forming a photoresist. The method may include forming the photoresist by mixing a sol-gel acrylic polymer-nanoparticles resin with a nanoparticles-dispersed acrylic resin. The sol-gel acrylic polymer-nanoparticles resin may be formed by mixing a monomer, a nanoparticle precursor, a coupling agent, a crosslinker and a photoinitiator in a sol-gel process. Each nanoparticle of a plurality of nanoparticles included in the photoresist may have a diameter selected from a range from 10 nm to 20 nm such that the photoresist is ultra-violet curable.

WO 2024/258344 A1

PHOTORESIST AND METHOD OF FORMING THE SAME, NANOIMPRINTING METHOD

CROSS-REFERENCE TO RELATED APPLICATION

[0001] This application claims the benefit of priority of Singapore application No. 10202301701R filed June 15, 2023, the contents of it being hereby incorporated by reference in its entirety for all purposes.

TECHNICAL FIELD

[0002] Various embodiments of this disclosure may relate to a photoresist. Various embodiments of this disclosure may relate to a method of forming a photoresist. Various embodiments of this disclosure may relate to a nanoimprinting method.

BACKGROUND

[0003] Ultraviolet (UV) nanoimprint lithography (NIL), a next-generation patterning technology that enables the creation of high-resolution nanostructures and provides a complementary option to conventional photolithography, has attracted increasing attention over the past decades. UV-NIL technology has been effectively applied in manufacturing advanced optics due to its simple, cost-effective, and high-throughput production procedures. For instance, UV-NIL technology has been applied in next generation waveguide optics, thin film encapsulation for organic light emitting diodes (LEDs), and microlens arrays for charge coupled devices (CCDs)/complementary metal oxide semiconductor sensors. FIG. 1A shows a schematic of a charge coupled device (CCD) without microlens and a charge coupled device (CCD) with microlens.

[0004] Despite the advantages of nanoimprint lithography technology, the availability of suitable photoresist materials is a crucial roadblock. So far, a significant fraction of conventional limpid polymers offers refractive indices (n) of less than 1.9, typically only varying from 1.4 to 1.6, which is far from being able to satisfy the demands in advanced optics. FIG. 1B is a plot of refractive index (RI) n (measured at wavelength of 633 nm) as a function of wavelength (in nanometer or nm) illustrating the different applications of various photoresists. The lack of high refractive index polymers (HRIP) may limit developments in displays, augmented reality (AR)/virtual reality (VR) applications, and advanced optical components. There is also a lack of HRIP for large area fabrication of micro- and nano-structures via NIL to address the demand for flat optics and photonic devices.

[0005] To achieve resins with a high refractive index, the chemical incorporation of high polarizable molar refraction organic substituents (e.g., halogen heteroatoms, rigid aromatic group, and siloxane) or inorganic nanoparticles (such as amorphous silicon ($n \sim 4.2$), TiO_2 ($n \sim 2.6$)) into classical transparent polymers are crucial. However, high refractive polymer/nanoparticle nanocomposites have a trade-off with extinction coefficient, which is generally at around 0.2 due to severe microphase separation and optical scattering between organic polymeric matrices and large-sized inorganic nanoparticles. Hence, it is desirable to develop a photoresist with high refractive index and extremely low extinction coefficient.

SUMMARY

[0006] Various embodiments may relate to a method of forming a photoresist. The method may include forming the photoresist by mixing a sol-gel acrylic polymer-nanoparticles resin with a nanoparticles-dispersed acrylic resin. The sol-gel acrylic polymer-nanoparticles resin may be formed by mixing a monomer, a nanoparticle precursor, a coupling agent, a crosslinker and a photoinitiator in a sol-gel process. Each nanoparticle of a plurality of nanoparticles

included in the photoresist may have a diameter selected from a range from 10 nm to 20 nm such that the photoresist is ultra-violet curable.

[0007] Various embodiments may relate to a photoresist. The photoresist may include a sol-gel acrylic polymer-nanoparticles resin. The photoresist may also include a nanoparticles-dispersed acrylic resin mixed with the sol-gel acrylic polymer-nanoparticles resin. The sol-gel acrylic polymer-nanoparticles resin may be formed by mixing a monomer, a nanoparticle precursor, a coupling agent, a crosslinker and a photoinitiator in a sol-gel process. Each nanoparticle of a plurality of nanoparticles included in the photoresist may have a diameter selected from a range from 10 nm to 20 nm such that the photoresist is ultra-violet curable.

[0008] Various embodiments may relate to a nanoimprinting method. The nanoimprinting method may include providing the photoresist as described herein onto a substrate. The nanoimprinting method may also include covering the photoresist using a mold such that the photoresist is molded under a predetermined temperature and a predetermined pressure. The method may further include providing ultraviolet light to cure the photoresist. The method may additionally include removing the mold after the photoresist is cured.

BRIEF DESCRIPTION OF THE DRAWINGS

[0009] In the drawings, like reference characters generally refer to the same parts throughout the different views. The drawings are not necessarily drawn to scale, emphasis instead generally being placed upon illustrating the principles of various embodiments. In the following description, various embodiments of the invention are described with reference to the following drawings.

FIG. 1A shows a schematic of a charge coupled device (CCD) without microlens and a charge coupled device (CCD) with microlens.

FIG. 1B is a plot of refractive index (RI) *n* (measured at wavelength of 633 nm) as a function of wavelength (in nanometer or nm) illustrating the different applications of various photoresists.

FIG. 2 is a general illustration of a method of forming a photoresist according to various embodiments.

FIG. 3 is a general illustration of a photoresist according to various embodiments.

FIG. 4 is a general illustration of a nanoimprinting method according to various embodiments.

FIG. 5A is a table showing the amounts of reactants and processing conditions to form a sample of a sol-gel acrylic polymer-titania (TiO_2) resin according to various embodiments.

FIG. 5B shows a schematic of the method of forming the titania (TiO_2) nanoparticle/sol-gel acrylic resin according to various embodiments and the method of forming micro- and nanostructures using the titania (TiO_2) nanoparticle/sol-gel acrylic resin according to various embodiments.

FIG. 6A shows a plot of refractive index *n* and extinction coefficient *k* as a function of wavelength (in nanometer or nm) illustrating the variation of the refractive index and the extinction coefficient of different compositions of the photoresist according to various embodiments over the visible spectrum.

FIG. 6B shows (a) a transmission electron microscopy (TEM) image (inset: magnified image) of the TiO_2 nanoparticle/sol-gel acrylic photoresist according to various embodiments; and (b) a transmission electron microscopy (TEM) image of the formed titania (TiO_2) nanoparticles (diameter ~ 20 nm) according to various embodiments.

FIG. 7 shows a table showing the nanoimprint process parameters according to various embodiments.

FIG. 8 shows (a1) optical microscopy image and (a2 – a3) scanning electron microscopy (SEM) images of the silicon master mold; and (b1) optical microscopy image and (b2 – b3) scanning

electron microscopy (SEM) images of the replicated soft mold according to various embodiments.

FIG. 9 shows (a1) an optical microscopy image and (a2 – a3) scanning electron microscopy (SEM) images of the nanoimprint on 90% titania (TiO_2) – sol-gel acrylic photoresist according to various embodiments; (b1) an optical microscopy image and (b2 – b3) scanning electron microscopy (SEM) images of the nanoimprint on 80% titania (TiO_2) – sol-gel acrylic photoresist according to various embodiments; and (c1) an optical microscopy image and (c2 – c3) scanning electron microscopy (SEM) images of the nanoimprint on 70% titania (TiO_2) – sol-gel acrylic photoresist according to various embodiments.

FIG. 10 shows (a) a schematic illustrating formation of poly-methyl methacrylate (PMMA)-titania (TiO_2) resist according to various embodiments; and (b) a schematic illustrating formation of poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) resist according to various embodiments.

FIG. 11A shows a table of reactants and conditions for synthesis of poly-methyl methacrylate (PMMA)-titania (TiO_2) resist and poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) resist according to various embodiments.

FIG. 11B shows a table of the parameters for nanoimprinting of poly-methyl methacrylate (PMMA)-titania (TiO_2) resist and poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) resist according to various embodiments.

FIG. 12 shows scanning electron microscopy (SEM) images of (a) pure poly-methyl methacrylate (PMMA); (b) poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) according to various embodiments (inset: zoomed out image); and (c) poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments (inset: zoomed out image).

FIG. 13A shows a plot of refractive index *n* as a function of wavelength (in nanometer or nm) illustrating the variation of refractive index of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) and poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments under different wavelengths.

FIG. 13B shows a plot of extinction coefficient *k* as a function of wavelength (in nanometer or nm) illustrating the variation of extinction coefficient of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) and poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments under different wavelengths.

FIG. 13C shows transmission electron microscopy (TEM) images of (a) poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) (inset: magnified image) and (b) poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) (inset: magnified image) according to various embodiments.

FIG. 14 shows (a) – (b) scanning electron microscopy (SEM) images of ultraviolet (UV) imprinted micropillars of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) according to various embodiments, with the inset showing the cross-sectional SEM image.

FIG. 15 shows a cross-sectional scanning electron microscopy (SEM) image of imprinted micro pillars of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) (tilted view) according to various embodiments.

FIG. 16 shows optical images of a color array of nanopillars with diameters from 250 nm to 500 nm and pitches from 550 nm to 800 nm of (a) the silicon mold; (b) an imprinted array on poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments; and (c) an imprinted array on poly-pentabromobenzylmethacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments coated with 20 nm thick layer of aluminum (Al).

FIG. 17 shows field effect scanning electron microscopy (FESEM) images of nanoimprinted color arrays of high refractive index resin poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments coated with 20 nm layer aluminum : (a) nanopillar arrays with varying geometry, *viz.*, diameters from 250 nm to 500 nm and pitches from 550 nm to 800 nm; (b) – (c) nanopillar array with diameter 350 nm in diameter and 700 nm in pitch.

FIG. 18 shows a table comparing the resist according to various embodiments and several conventional resists for benchmarking.

DESCRIPTION

[0010] The following detailed description refers to the accompanying drawings that show, by way of illustration, specific details and embodiments in which the invention may be practiced. These embodiments are described in sufficient detail to enable those skilled in the art to practice the invention. Other embodiments may be utilized and structural, logical, and electrical changes may be made without departing from the scope of the invention. The various embodiments are not necessarily mutually exclusive, as some embodiments can be combined with one or more other embodiments to form new embodiments.

[0011] Features that are described in the context of an embodiment may correspondingly be applicable to the same or similar features in the other embodiments. Features that are described in the context of an embodiment may correspondingly be applicable to the other embodiments, even if not explicitly described in these other embodiments. Furthermore, additions and/or combinations and/or alternatives as described for a feature in the context of an embodiment may correspondingly be applicable to the same or similar feature in the other embodiments.

[0012] In the context of various embodiments, the articles "a", "an" and "the" as used with regard to a feature or element include a reference to one or more of the features or elements.

[0013] In the context of various embodiments, the term "about" or "approximately" as applied to a numeric value encompasses the exact value and a reasonable variance, e.g. within 10% of the specified value.

[0014] As used herein, the term "and/or" includes any and all combinations of one or more of the associated listed items.

[0015] By "comprising" it is meant including, but not limited to, whatever follows the word "comprising". Thus, use of the term "comprising" indicates that the listed elements are required or mandatory, but that other elements are optional and may or may not be present.

[0016] By "consisting of" is meant including, and limited to, whatever follows the phrase "consisting of". Thus, the phrase "consisting of" indicates that the listed elements are required or mandatory, and that no other elements may be present.

[0017] Embodiments described in the context of one of the photoresists are analogously valid for the other photoresists, embodiments described in the context of a method are analogously valid for a photoresist, and vice versa.

[0018] Various embodiments may address issues faced by conventional photoresists.

[0019] FIG. 2 is a general illustration of a method of forming a photoresist according to various embodiments. The method may include, in 202, forming the photoresist by mixing a sol-gel acrylic polymer-nanoparticles resin with a nanoparticles-dispersed acrylic resin. The sol-gel acrylic polymer-nanoparticles resin may be formed by mixing a monomer, a nanoparticle precursor, a coupling agent, a crosslinker and a photoinitiator in a sol-gel process. Each nanoparticle of a plurality of nanoparticles included in the photoresist may have a diameter selected from a range from 10 nm to 20 nm such that the photoresist is ultra-violet curable.

[0020] In other words, the method may relate to forming a photoresist (also referred to as a photoresist mixture) by mixing a sol-gel acrylic polymer-nanoparticles resin and an

nanoparticles-dispersed acrylic resin. Each nanoparticle in the photoresist may be of a range from 10 nm to 20 nm.

[0021] In various embodiments, the photoresist may have a high refractive index, e.g., up to 2. In various embodiments, the photoresist may have a refractive index selected from a range from 1.9 to 2 under visible light (e.g., under a wavelength selected from a range from 400 nm to 550 nm). In various embodiments, the photoresist may have a low extinction coefficient. In various embodiments, the photoresist may have an extinction coefficient of 0 or close to 0, e.g., under visible light or spectrum (e.g., under a wavelength selected from a range from 400 nm to 700 nm). For instance, the photoresist may have an extinction coefficient of less than 0.1 e.g., less than or equal to 0.01, e.g., 0.

[0022] Various embodiments may relate to a photoresist which has a high refractive index and a low extinction coefficient. The method as described herein may result in a photoresist with high loading of small nanoparticles (from 10 nm to 20 nm), thereby resulting in the photoresist having a high refractive index and a low extinction coefficient. Further, by addition of nanoparticles-dispersed acrylic resin, high-temperature treatment, which is incompatible with the microelectronic fabrication process, may not be required to achieve a high refractive index. The shrinkage of nanostructures, e.g., nanopillars via high-temperature process may be difficult to control, which affects the fabrication accuracy.

[0023] In various embodiments, the nanoparticle precursor forming the sol-gel acrylic polymer-nanoparticles resin may be a titania precursor. In various embodiments, the plurality of nanoparticles may be titania (TiO_2) nanoparticles. A first portion of the titania (TiO_2) nanoparticles may be formed from the titania precursor of the sol-gel acrylic polymer-nanoparticles resin. A second portion of the titania (TiO_2) nanoparticles may be from the nanoparticles-dispersed acrylic resin.

[0024] The nanoparticles-dispersed acrylic resin may include the second portion of the titania (TiO_2) nanoparticles dispersed in an acrylic resin. In other words, the nanoparticles-dispersed acrylic resin may include an acrylic resin mixed with TiO_2 nanoparticles.

[0025] The first portion of the titania (TiO_2) nanoparticles may be covalently bonded to a surrounding polymer matrix. In other words, the sol-gel acrylic polymer-nanoparticles resin may include a polymer matrix with TiO_2 nanoparticles bonded to the polymer matrix.

[0026] The nanoparticles in the photoresist may originate from both the nanoparticles-dispersed acrylic resin and the sol-gel acrylic polymer-nanoparticles resin. The nanoparticles as described herein may have any suitable shape, e.g. spherical shape, cuboid shape or irregular shape.

[0027] In various embodiments, the nanoparticles-dispersed acrylic resin may be a TiO_2 nanoparticle dispersed acrylic resin, while the sol-gel acrylic polymer-nanoparticles resin may be a sol-gel acrylic polymer-TiO_2 resin. The resultant photoresist may be TiO_2 nanoparticle/sol-gel acrylic resin. The TiO_2 nanoparticle/sol-gel acrylic resin may be homogenized with water bath sonication (e.g., for 15 minutes) before being used for nanoimprinting.

[0028] In various embodiments, the photoresist may have a loading of nanoparticles (e.g., TiO_2 nanoparticles) of 70 wt.% or more (relative to weight of photoresist), e.g., 80 wt.% or more (relative to weight of photoresist), e.g., 90 wt.% or more (relative to weight of photoresist). A higher loading of TiO_2 nanoparticles may lead to a higher refractive index n.

[0029] In various embodiments, the coupling agent forming the sol-gel acrylic polymer-nanoparticles resin may be trimethoxy(7-octen-1-yl)silane.

[0030] In various embodiments, the monomer forming the sol-gel acrylic polymer-nanoparticles resin is methyl-methacrylate (MMA).

[0031] In various embodiments, the crosslinker forming the sol-gel acrylic polymer-nanoparticles resin may be poly (ethylene glycol) dimethacrylate (PEGD).

[0032] In various embodiments, the photoinitiator forming the sol-gel acrylic polymer-nanoparticles resin may be dimethoxyphenyl acetophenone (DPAP).

[0033] The sol-gel acrylic polymer-nanoparticles resin may be an acrylate-based polymer-titanium oxide nanocomposite. The sol-gel acrylic polymer-nanoparticles resin may be an unitary chemical grafting system. High concentrations of sol-gel grafting active substituents, such as -Si-(O-CH_3-)$_3$, may be introduced (via the coupling agent) into the acrylic polymer chain.

[0034] In various embodiments, the sol-gel acrylic polymer-nanoparticles resin may be formed by mixing the monomer, the nanoparticle precursor, the coupling agent, the crosslinker and the photoinitiator via magnetic agitation at a temperature selected from a range from 20°C to 25°C.

[0035] In various embodiments, the sol-gel acrylic polymer-nanoparticles resin and the nanoparticles-dispersed acrylic resin may be free of or devoid of any solvent or plasticizer.

[0036] In various embodiments, the photoresist may be formed by mixing the sol-gel acrylic polymer-nanoparticles resin with the nanoparticles-dispersed acrylic resin in a weight ratio of 1 : 9.

[0037] In various embodiments, the photoresist may be formed by mixing the sol-gel acrylic polymer-nanoparticles resin with the nanoparticles-dispersed acrylic resin in a weight ratio of 2 : 8.

[0038] In various embodiments, the photoresist may be formed by mixing the sol-gel acrylic polymer-nanoparticles resin with the nanoparticles-dispersed acrylic resin in a weight ratio of 3 : 7.

[0039] Various embodiments may relate to a photoresist formed by any method as described herein.

[0040] FIG. 3 is a general illustration of a photoresist according to various embodiments. The photoresist may include a sol-gel acrylic polymer-nanoparticles resin 302. The photoresist may also include a nanoparticles-dispersed acrylic resin 304 mixed with the sol-gel acrylic polymer-nanoparticles resin 302. The sol-gel acrylic polymer-nanoparticles resin 302 may be formed by mixing a monomer, a nanoparticle precursor, a coupling agent, a crosslinker and a photoinitiator in a sol-gel process. Each nanoparticle of a plurality of nanoparticles included in the photoresist may have a diameter selected from a range from 10 nm to 20 nm such that the photoresist is ultra-violet curable.

[0041] In other words, the photoresist may be a mixture of a sol-gel acrylic polymer-nanoparticles resin 302 and a nanoparticles-dispersed acrylic resin 304. The photoresist may have nanoparticles in the range from 10 nm to 20 nm.

[0042] In various embodiments, the sol-gel acrylic polymer-nanoparticles resin 302 may be mixed with the nanoparticles-dispersed acrylic resin 304 in a weight ratio of 1 : 9.

[0043] In various embodiments, the sol-gel acrylic polymer-nanoparticles resin 302 may be mixed with the nanoparticles-dispersed acrylic resin 304 in a weight ratio of 2 : 8.

[0044] In various embodiments, the sol-gel acrylic polymer-nanoparticles resin 302 may be mixed with the nanoparticles-dispersed acrylic resin 304 in a weight ratio of 3 : 7.

[0045] FIG. 4 is a general illustration of a nanoimprinting method according to various embodiments. The nanoimprinting method may include, in 402, providing the photoresist as described herein onto a substrate. The nanoimprinting method may also include, in 404, covering the photoresist using a mold such that the photoresist is molded under a predetermined temperature and a predetermined pressure. The method may further include, in 406, providing ultraviolet light to cure the photoresist. The method may additionally include, in 408, removing the mold after the photoresist is cured.

[0046] In various embodiments, the predetermined pressure may be any suitable pressure, e.g. any suitable pressure selected from a range from 1 bar to 3 bars, e.g., atmospheric pressure (about 1 bar). In various embodiments, the predetermined temperature may be any suitable temperature, such as any temperature selected from a range from 30 °C to 70 °C , e.g., 50 °C.

[0047] In various embodiments, the photoresist may be provided onto the substrate by any suitable deposition method, such as drop-casting or coating. By covering the photoresist using the mold under the predetermined temperature and the predetermined pressure, the photoresist may conform to the shape determined by the mold.

[0048] In various embodiments, by providing the ultraviolet light, the photoresist may be cured via a photo-initiated radical copolymerization reaction. The photoinitiator present in the photoresist may help to start the reaction.

[0049] In various embodiments, the mold been removed may refer to separating the mold and the cured photoresist. The demolding may be carried out at any suitable temperature, e.g., at or below room temperature.

[0050] As mentioned above, a significant fraction of conventional limpid polymers offers refractive indices (n) only varying from 1.4 to 1.6, which is far from satisfying demands in advanced optics. To achieve resins with a high refractive index, the chemical incorporation of the high polarizable molar refraction organic substituents (e.g., halogen heteroatoms, rigid aromatic group, and siloxane) or inorganic nanoparticles (such as amorphous silicon ($n \sim 4.2$), TiO_2 ($n \sim 2.6$)) into classical transparent polymers are crucial. These methodologies are motivated by the effective-medium-model ($N \sim N_{particle} * \Phi_{particle} + N_{matrix} * \Phi_{matrix}$), which predicts the average refractive indices of resins N to be a volume average of the components. In this regard, $\Phi_{particle}$ may be the volume proportion of particles, Φ_{matrix} may be the volume proportion of the matrix, $N_{particle}$ may be the refractive index of the particles, and N_{matrix} may be the refractive index of the matrix.

[0051] The incorporation of organic substituents may bring about photo-thermal stability reduction and multistage complex synthesis steps. On the other hand, high refractive polymer/nanoparticle nanocomposites may have a trade-off with extinction coefficient (k), which is generally at about 0.2 as a result of the severe microphase separation and optical scattering between organic polymeric matrices and large sized inorganic nanoparticles. This may call for completely miscible nanocomposites, i.e., homogenous distribution of filler particles in the polymer matrices over extremely high nanoparticle loading without serious aggregation, to achieve the highest n and lowest k. Homogeneous dispersion of ultra-small nanoparticles in polymer matrices via *in situ* sol-gel processing method was developed to resolve the above issues effectively. The resin may then be used to nanoimprint to test its imprint ability to create patterns with high definition and throughput. However, there is still a big challenge in increasing the particle's grafting efficiency and decreasing their spatial size simultaneously. Various embodiments may introduce a high concentration of sol-gel grafting active substituents, such as -OH and -Si-(O-CH_3-)$_3$, into the polymer chain and may then combine it with the TiO_2 dispersed acrylic resin. Thus, the chemical grafted acrylic polymer TiO_2 photoresist may act as both surfactant and matrix concurrently, creating a polymer-supported dispersion of inorganic nanoparticles under *in situ* sol-gel grafting manner with high nanoparticle loading and small diameter of ~10 nm - 20 nm.

[0052] Experiment A relates to formation of a photoresist with addition of nanoparticles-dispersed acrylic resin, while Experiment B relates to formation of a photoresist without addition of nanoparticles-dispersed acrylic resin. Without the addition of nanoparticles-dispersed acrylic resin, high-temperature treatment may be required to achieve a high refractive index, which is not compatible with the microelectronic fabrication process. The shrinkage of nanostructures e.g., nanopillars, via high-temperature process may be difficult to control, which affects the fabrication accuracy.

[0053] Experiment A

[0054] Synthesis of sol-gel acrylic polymer-TiO_2 resin

[0055] A sol-gel acrylic polymer-TiO_2 resin sample may be formed by using the amounts of reactants and processing conditions as shown in FIG. 5A. FIG. 5A is a table showing the amounts of reactants and processing conditions to form a sample of a sol-gel acrylic polymer-titania (TiO_2) resin according to various embodiments. All chemicals were purchased from Sigma-Aldrich. The MMA (monomer), TI (titania precursor), TS (coupling agent), PEGD (crosslinker), and DPAP (photoinitiator) were mixed into one uniform sol mixture by vigorous magnetic agitating at room temperature.

[0056] Preparation of TiO_2 nanoparticle/sol-gel acrylic photoresist

[0057] The TiO_2 nanoparticle/sol-gel acrylic resin was prepared by mixing TiO_2 nanoparticle dispersed acrylic resin and sol-gel acrylic polymer-TiO_2 resin at designed weight ratios (9 : 1, 8 : 2, and 7 : 3, respectively). Then, the mixture was homogenized with water bath sonication for 15 min for imprint use.

[0058] FIG. 5B shows a schematic of the method of forming the titania (TiO_2) nanoparticle/sol-gel acrylic resin according to various embodiments and the method of forming micro- and nanostructures using the titania (TiO_2) nanoparticle/sol-gel acrylic resin according to various embodiments. The synthesis of dielectric high refractive and low loss resins may evolve from the acrylate-based polymer-titanium oxide nanocomposites via the sol-gel approach. The combination of sol-gel prepared acrylate-based polymer-titanium oxide nanocomposites and TiO_2 nanoparticle dispersed acrylic resins may result in TiO_2 nanoparticle/sol-gel acrylic photoresist. The TiO_2 nanoparticle/sol-gel acrylic photoresist can be applied for nanoimprinting lithography (NIL) to make large-area patterns at nano-meter scales for advanced optics, with advantages such as great nanoimprint capability, high refractive

index and extremely low extinction coefficient, solvent-free, decent fidelity with low shrinkage and high material integrity with nanoparticle-sol gel in-situ linkage over other TiO_2-based resin.

[0059] The refractive index (n) and extinction coefficient (k) of the TiO_2 nanoparticle/sol-gel acrylic photoresists were characterized with an ellipsometer. FIG. 6A shows a plot of refractive index n and extinction coefficient k as a function of wavelength (in nanometer or nm) illustrating the variation of the refractive index and the extinction coefficient of different compositions of the photoresist according to various embodiments over the visible spectrum. The photoresists may have different TiO_2/sol-gel weight ratios of 90%, 80% and 70%, respectively. In the wavelength range of 420 nm to 700 nm, the value of n gradually reduces from ~2.0 to 1.83. Among the three nanocomposites, the resin with a 90% weight ratio exhibits the highest n, around 1.9 ~ 2.0, in the visible regime. It can be observed that n drops when the weight ratio reduces. In addition, the extinction coefficient k remains at zero for all three nanocomposites. The results validate that a high refractive index and extremely low extinction coefficient may be achieved. FIG. 6B shows (a) a transmission electron microscopy (TEM) image (inset: magnified image) of the TiO_2 nanoparticle/sol-gel acrylic photoresist according to various embodiments; and (b) a transmission electron microscopy (TEM) image of the formed titania (TiO_2) nanoparticles (diameter ~ 20 nm) according to various embodiments. Various embodiments may relate to a solvent free approach to achieve high nanoparticle loading and small spatial size (diameter: 10 nm - 20 nm) simultaneously.

[0060] A NIL process may be applied to test the nanoimprint capability for the designed TiO_2 nanoparticle/sol-gel acrylic photoresist. FIG. 7 shows a table showing the nanoimprint process parameters according to various embodiments. The photoresist may be drop-casted on a silicon wafer or quartz substrate and may then get covered by the NIL mold timely. The photoresist may then flow into the NIL mold fully under certain pressure and temperature. The imprinted photoresist may get *in-situ* cured completely by sustaining the photo-initiated radical

copolymerization imposed by the successive ultraviolet radiation exposure. The cured photoresist may be demolded at room temperature.

[0061] FIG. 8 shows (a1) optical microscopy image and (a2 – a3) scanning electron microscopy (SEM) images of the silicon master mold; and (b1) optical microscopy image and (b2 – b3) scanning electron microscopy (SEM) images of the replicated soft mold according to various embodiments. First, the TiO_2 nanoparticle/sol-gel acrylic photoresist was drop casted on top of the adhesion layer of the quartz substrate, and the silicon master mold may be applied onto the deposited photoresist. The resin was then heated at 50°C for 120s, followed by UV curing for 360s (in 5s On/Off cycle), which was applied to solidify the TiO_2 nanoparticle/sol-gel acrylic resin. The pressure was set to 1.0 bar. The soft mold (of the cured photoresist) formed may then be used to fabricate metalenses.

[0062] FIG. 9 shows (a1) an optical microscopy image and (a2 – a3) scanning electron microscopy (SEM) images of the nanoimprint on 90% titania (TiO_2) – sol-gel acrylic photoresist according to various embodiments; (b1) an optical microscopy image and (b2 – b3) scanning electron microscopy (SEM) images of the nanoimprint on 80% titania (TiO_2) – sol-gel acrylic photoresist according to various embodiments; and (c1) an optical microscopy image and (c2 – c3) scanning electron microscopy (SEM) images of the nanoimprint on 70% titania (TiO_2) – sol-gel acrylic photoresist according to various embodiments. The results validate that the developed TiO_2 nanoparticle/sol-gel acrylic photoresist may show great capability in nanoimprint applications.

[0063] The sol-gel grafted TiO_2-acrylic polymers may provide a polymer-supported dispersion of TiO_2 nanoparticles with high nanoparticle loading and small diameter ~10 nm - 20 nm. The developed TiO_2 nanoparticle/sol-gel acrylic resins may have high refractive index (1.90 ~ 2.0) and extremely low extinction coefficients (~0). The developed TiO_2 nanoparticle/sol-gel acrylic resins may demonstrate great capability for nanoimprinting. High

concentration of sol-gel grafting active substituents, such as -Si-(O-CH_3-)$_3$, may be introduced into the acrylic polymer chain. It may then be combined with the TiO_2 nanoparticle dispersed acrylic resin to form nanoimprintable TiO_2 nanoparticle/sol-gel acrylic photoresist. The high refractive index nanoimprintable TiO_2 nanoparticle/sol-gel acrylic photoresist may be suitable for nanoimprinting of optical nanostructures, flat optics for advanced optical applications (e.g. to reduce size of conventional optical devices, forming high quality augmented reality/virtual reality (AR/VR) devices). The high refractive index of the photoresist may enable miniaturization of conventional optics and thereby reduce the overall device size.

[0064] Experiment B

[0065] FIG. 10 shows (a) a schematic illustrating formation of poly-methyl methacrylate (PMMA)-titania (TiO_2) resist according to various embodiments; and (b) a schematic illustrating formation of poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) resist according to various embodiments.

[0066] In FIG. 10(a), methyl methacrylate (MMA, monomer), titanium isopropoxide (TI, titania precursor), trimethoxy(7-octen-1-yl)silane (TS, coupling agent), poly(ethylene glycol dimethacrylate) (PEGD, crosslinker), and dimethoxy phenylacetophenone (DPAP, photoinitiator) may be combined into one uniform sol mixture by vigorous magnetic agitating at room temperature. Then, the soliquid may be spin-coated on a silicon wafer and may *in-situ* get cured by sustaining the photo-initiated radical copolymerization imposed by the ultraviolet radiation to synthesize the trimethoxysilane tailored PMMA-graft-titanium as a thin film. Subsequently, the PMMA-TiO_2 thin film may be prepared followed by 1 hour baking at 80 °C to enable the intact transition of titanium to TiO_2.

[0067] In FIG. 10(b), hydroxyl-substituted pentabromobenzyl methacrylate (BMA, monomer), titanium isopropoxide (TI, titania precursor), trimethoxy(7-octen-1- yl)silane (TS, coupling agent), poly(ethylene glycol dimethacrylate) (PEGD, crosslinker), and dimethoxy

phenylacetophenone (DPAP, photoinitiator) may be combined into one uniform sol mixture by vigorous magnetic agitating at room temperature. Then, the soliquid may be spin-coated on a silicon wafer and may *in-situ* get cured by sustaining the photo-initiated radical copolymerization imposed by the ultraviolet radiation to synthesize the trimethoxysilane tailored PBMA-graft-titanium as a thin film. Subsequently, the PBMA-TiO_2 thin film may be prepared followed by 1 hour baking at 80 °C to enable the intact transition of titanium to TiO_2 for further optical property examination. In this regard, ultraviolet radiation imprint for PMMA-TiO_2 and PBMA -TiO_2 by using micro-featured negative-type molds may be developed. The process may be developed and optimized as a two-step ultraviolet radiation imprint: i) 10 bars, 80 °C, 5 min. ii) 5 min ultraviolet radiation exposure. FIG. 11A shows a table of reactants and conditions for synthesis of poly-methyl methacrylate (PMMA)-titania (TiO_2) resist and poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) resist according to various embodiments. FIG. 11B shows a table of the parameters for nanoimprinting of poly-methyl methacrylate (PMMA)-titania (TiO_2) resist and poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) resist according to various embodiments.

[0068] Various embodiments may relate to a method of forming a photoresist by mixing a monomer, a nanoparticle precursor, a coupling agent, a cross-linker and a photoinitiator in a sol-gel process. The photoresist may include a plurality of nanoparticles, such that each nanoparticle of the plurality of nanoparticles has a diameter selected from a range from 10 nm to 20 nm. Various embodiments may relate to a photoresist formed by such a method.

[0069] By controlling the titanium amount for the polymerization system, the corresponding titania content in the smooth PMMA-TiO_2 and PBMA-TiO_2 thin films may be 64.6 weight percent (wt. %) and 69.2 weight percent (wt. %), respectively. The surface roughness and particle size of the TiO_2 segment of the prepared acrylic resins thin films may be characterized by SEM images. FIG. 12 shows scanning electron microscopy (SEM) images of (a) pure poly-

methyl methacrylate (PMMA); (b) poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) according to various embodiments (inset: zoomed out image); and (c) poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments (inset: zoomed out image). No apparent big sized TiO_2 particle emerges in the surfaces of the acrylic resin (FIGS. 12(b)-(c)), and the integrated surface roughness only differs slightly from the smooth surface of pure PMMA film (FIG. 12(a)), which implies the promising compatibility between acrylate-based polymer matrix and TiO_2 particles in the prepared thin films with such excellent surface planarity.

[0070] The refractive indices (n) and extinction coefficients (k) distributions of the acrylic resins thin films in the wavelength range are measured by ellipsometry and the results are plotted in FIGS. 13A-B. FIG. 13A shows a plot of refractive index n as a function of wavelength (in nanometer or nm) illustrating the variation of refractive index of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) and poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments under different wavelengths. FIG. 13B shows a plot of extinction coefficient k as a function of wavelength (in nanometer or nm) illustrating the variation of extinction coefficient of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) and poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments under different wavelengths. The n value at 532 nm of PMMA-TiO_2 and PBMA-TiO_2 thin films may be around 1.92 and 1.93, respectively. Overall, this investigation demonstrates that the acrylic resins thin films may have improved high refractive indices exceeding 1.9 in the broadband visible regime (FIG. 13A). Further, FIG. 13B shows the k values approaching 0.01 for all the prepared acrylic resins thin films in the wavelength ranging from 400 to 900 nm, which proposes good optical transparency in the visible region. With such optical properties and planar smooth surfaces, this type of acrylic resins may be suitable for making nano-micro

sized structures for applications of advanced optics such as structural coloration and holographic displays. FIG. 13C shows transmission electron microscopy (TEM) images of (a) poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) (inset: magnified image) and (b) poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) (inset: magnified image) according to various embodiments. Various embodiments may relate to a solvent free approach to achieve high nanoparticles loading (about 64% – 69%) and small spatial size (diameter of about 10 nm – 20 nm) simultaneously.

[0071] FIG. 14 shows (a) – (b) scanning electron microscopy (SEM) images of ultraviolet (UV) imprinted micropillars of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) according to various embodiments, with the inset showing the cross-sectional SEM image. The SEM images demonstrate the microimprint ability of the acrylic resins thin films, which may result in micropillar arrays with good pattern fidelity. The diameter and pitch of the micropillars array are ~1 and ~2 um obtained using high refractive index resin of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %). FIG. 15 shows a cross-sectional scanning electron microscopy (SEM) image of imprinted micro pillars of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) (tilted view) according to various embodiments. The cross-sectional SEM image of poly-methyl methacrylate (PMMA)-titania (TiO_2) (TiO_2: 64.6 wt. %) nanoimprinted acrylic resin thin film shows the residual layer thickness and pillar heights are ~ 10 nm and ~ 1 μm, respectively.

[0072] Structural color arrays are designed in order to demonstrate the application of the high refractive index resin for anti-counterfeiting. Arrays with nanopillars were patterned onto silicon to make the mold. The pattern may then be transferred to a soft mold and imprinted onto poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) to form imprinted nanopillars.

[0073] FIG. 16 shows optical images of a color array of nanopillars with diameters from 250 nm to 500 nm and pitches from 550 nm to 800 nm of (a) the silicon mold; (b) an imprinted array on poly-pentabromobenzyl methacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments; and (c) an imprinted array on poly-pentabromobenzylmethacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments coated with 20 nm thick layer of aluminum (Al). Colors can be observed from the imprinted array due to the dielectric nano-resonators (FIG. 16(b)). Upon coating a thin layer of aluminum (20 nm thick), more colors can be generated based on plasmonic resonance. When compared with traditional printed colors using chemical pigments, nanostructured colors may exhibit the following advantages: (1) higher resolution, (2) brighter colors under sunlight, (3) better durability, and (4) dynamic tuning by changing the surface morphology.

[0074] FIG. 17 shows field effect scanning electron microscopy (FESEM) images of nanoimprinted color arrays of high refractive index resin poly-pentabromobenzylmethacrylate (PBMA)-titania (TiO_2) (TiO_2: 69.2 wt. %) according to various embodiments coated with 20 nm layer aluminum : (a) nanopillar arrays with varying geometry, *viz.*, diameters from 250 nm to 500 nm and pitches from 550 nm to 800 nm; (b) – (c) nanopillar array with diameter 350 nm in diameter and 700 nm in pitch. The SEM images show the nanoimprintability of the acrylic resins, which results in nanopillar arrays with good pattern fidelity. FIG. 18 shows a table comparing the resist according to various embodiments and several conventional resists for benchmarking.

[0075] The polymer systems may have two kinds of grafting active substituents (-OH and -Si-(O-CH_3-)$_3$) in the macromolecular chain and employ *in-situ* formation of TiO_2 nanoparticles as inorganic high refractive index feedstock to achieve high refractive index (n ~1.95) and low extinction coefficient (k ~0.01) in the visible spectrum (wavelength from 400nm to 700nm).

[0076] The *in-situ* formation of TiO_2 nanoparticles may be chemically grafted on the resin matrices without using any solvent, which may realize the high nanoparticle loading (64%-69%) and small spatial size (diameter: 10 nm - 20 nm) simultaneously, leading to the achievement of the high *n* and low *k* in the visible domain. The precursor (trimethoxy(7-octen-1-yl)silane) for the grafting active substituent $Si\text{-}(O\text{-}CH_3\text{-})_3$ may have a longer and more simplified molecular side chain to decrease steric hindrance during co-polymerization and increase nanoparticles grafting efficiency. The enhanced nanoparticles grafting efficiency may realize the higher nanoparticle loading (such as: 69.2%) and smaller spatial size (diameter: 10 nm - 20 nm) simultaneously, which further leads to the achievement of the high *n* and low *k* in the visible domain.

[0077] The developed chemically grafted acrylic polymer-TiO_2 resins may contain abundant carbon-carbon double bonds, which are ultraviolet curable. The resins may be feasible for UV nanoimprint lithography and may be able to achieve high pattern fidelity with ~10 nm thick residual layer. The optically active transparent acrylic resins can undergo UV radiation imprint with extremely good reliability and reiterative pattern-clone performance. The double bond may cater to various requirements for scaling up. Also, there may have potential for applications with require no or minimal residual layer. Various embodiments (e.g. nano-pillar arrays) may be manufactured through a one-step relative cost-effective imprint.

[0078] Various embodiments may have high transparency and efficiency, lower loss optical materials for advanced optics and photonics compared with low refractive index polymers. Various embodiments may allow wider field of view and larger deflection angle for the next generation of diffractive optical elements for AR/VR devices. Various embodiments may be suitable for making micro- and nanostructures via nanoimprint lithography with a thin residual layer (~10 nm thickness) for flat optical components and other optical components.

Claims

1. A method of forming a photoresist, the method comprising:
   forming the photoresist by mixing a sol-gel acrylic polymer-nanoparticles resin with a nanoparticles-dispersed acrylic resin;
   wherein the sol-gel acrylic polymer-nanoparticles resin is formed by mixing a monomer, a nanoparticle precursor, a coupling agent, a crosslinker and a photoinitiator in a sol-gel process; and
   wherein each nanoparticle of a plurality of nanoparticles included in the photoresist has a diameter selected from a range from 10 nm to 20 nm such that the photoresist is ultra-violet curable.

2. The method according to claim 1,
   wherein the nanoparticle precursor forming the sol-gel acrylic polymer-nanoparticles resin is a titania precursor.

3. The method according to claim 2,
   wherein the plurality of nanoparticles is titania (TiO_2) nanoparticles;
   wherein a first portion of the titania (TiO_2) nanoparticles is formed from the titania precursor of the sol-gel acrylic polymer-nanoparticles resin; and
   wherein a second portion of the titania (TiO_2) nanoparticles is from the nanoparticles-dispersed acrylic resin.

4. The method according to claim 3,
   wherein the nanoparticles-dispersed acrylic resin includes the second portion of the titania (TiO_2) nanoparticles dispersed in an acrylic resin.

5. The method according to claim 3,
   wherein the first portion of the titania (TiO_2) nanoparticles is covalently bonded to a surrounding polymer matrix.

6. The method according to claim 1,

wherein the coupling agent forming the sol-gel acrylic polymer-nanoparticles resin is trimethoxy(7-octen-1-yl)silane.

7. The method according to claim 1,
wherein the monomer forming the sol-gel acrylic polymer-nanoparticles resin is methyl-methacrylate (MMA);
wherein the crosslinker forming the sol-gel acrylic polymer-nanoparticles resin is poly (ethylene glycol) dimethacrylate (PEGD); and
wherein the photoinitiator forming the sol-gel acrylic polymer-nanoparticles resin is dimethoxyphenyl acetophenone (DPAP).

8. The method according to claim 1,
wherein the sol-gel acrylic polymer-nanoparticles resin is formed by mixing the monomer, the nanoparticle precursor, the coupling agent, the crosslinker and the photoinitiator via magnetic agitation at a temperature selected from a range from 20°C to 25°C.

9. The method according to claim 1,
wherein the sol-gel acrylic polymer-nanoparticles resin and the nanoparticles-dispersed acrylic resin are free of any solvent or plasticizer.

10. The method according to claim 1,
wherein the photoresist is formed by mixing the sol-gel acrylic polymer-nanoparticles resin with the nanoparticles-dispersed acrylic resin in a weight ratio of 1 : 9.

11. The method according to claim 1,
wherein the photoresist is formed by mixing the sol-gel acrylic polymer-nanoparticles resin with the nanoparticles-dispersed acrylic resin in a weight ratio of 2 : 8.

12. The method according to claim 1,

wherein the photoresist is formed by mixing the sol-gel acrylic polymer-nanoparticles resin with the nanoparticles-dispersed acrylic resin in a weight ratio of 3 : 7.

13. The method according to claim 1,

wherein the photoresist has a refractive index selected from a range from 1.9 to 2 under visible light.

14. The method according to claim 1,

wherein the photoresist has an extinction coefficient of 0.

15. A photoresist comprising:

a sol-gel acrylic polymer-nanoparticles resin; and

a nanoparticles-dispersed acrylic resin mixed with the sol-gel acrylic polymer-nanoparticles resin;

wherein the sol-gel acrylic polymer-nanoparticles resin is formed by mixing a monomer, a nanoparticle precursor, a coupling agent, a crosslinker and a photoinitiator in a sol-gel process; and

wherein each nanoparticle of a plurality of nanoparticles included in the photoresist has a diameter selected from a range from 10 nm to 20 nm such that the photoresist is ultra-violet curable.

16. The photoresist according to claim 15,

wherein the sol-gel acrylic polymer-nanoparticles resin is mixed with the nanoparticles-dispersed acrylic resin in a weight ratio of 1 : 9.

17. The photoresist according to claim 15,

wherein the sol-gel acrylic polymer-nanoparticles resin is mixed with the nanoparticles-dispersed acrylic resin in a weight ratio of 2 : 8.

18. The photoresist according to claim 15,

wherein the sol-gel acrylic polymer-nanoparticles resin is mixed with the nanoparticles-dispersed acrylic resin in a weight ratio of 3 : 7.

19. The photoresist according to claim 15,

wherein the photoresist is configured to be used in nanoimprint lithography (NIL).

20. A nanoimprinting method comprising:

providing a photoresist onto a substrate;

covering the photoresist using a mold such that the photoresist is molded under a predetermined temperature and a predetermined pressure;

providing ultraviolet light to cure the photoresist; and

removing the mold after the photoresist is cured;

wherein the photoresist comprises:

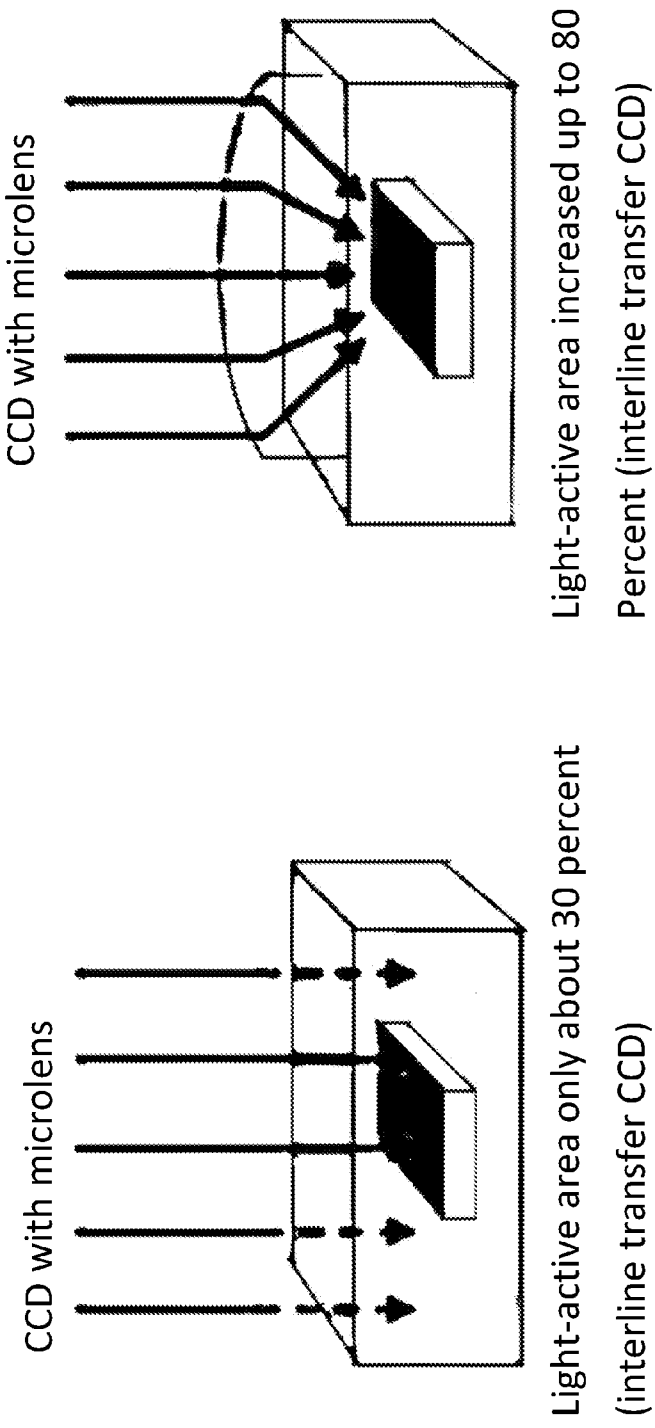
a sol-gel acrylic polymer-nanoparticles resin; and

a nanoparticles-dispersed acrylic resin mixed with the sol-gel acrylic polymer-nanoparticles resin;

wherein the sol-gel acrylic polymer-nanoparticles resin is formed by mixing a monomer, a nanoparticle precursor, a coupling agent, a crosslinker and a photoinitiator in a sol-gel process; and

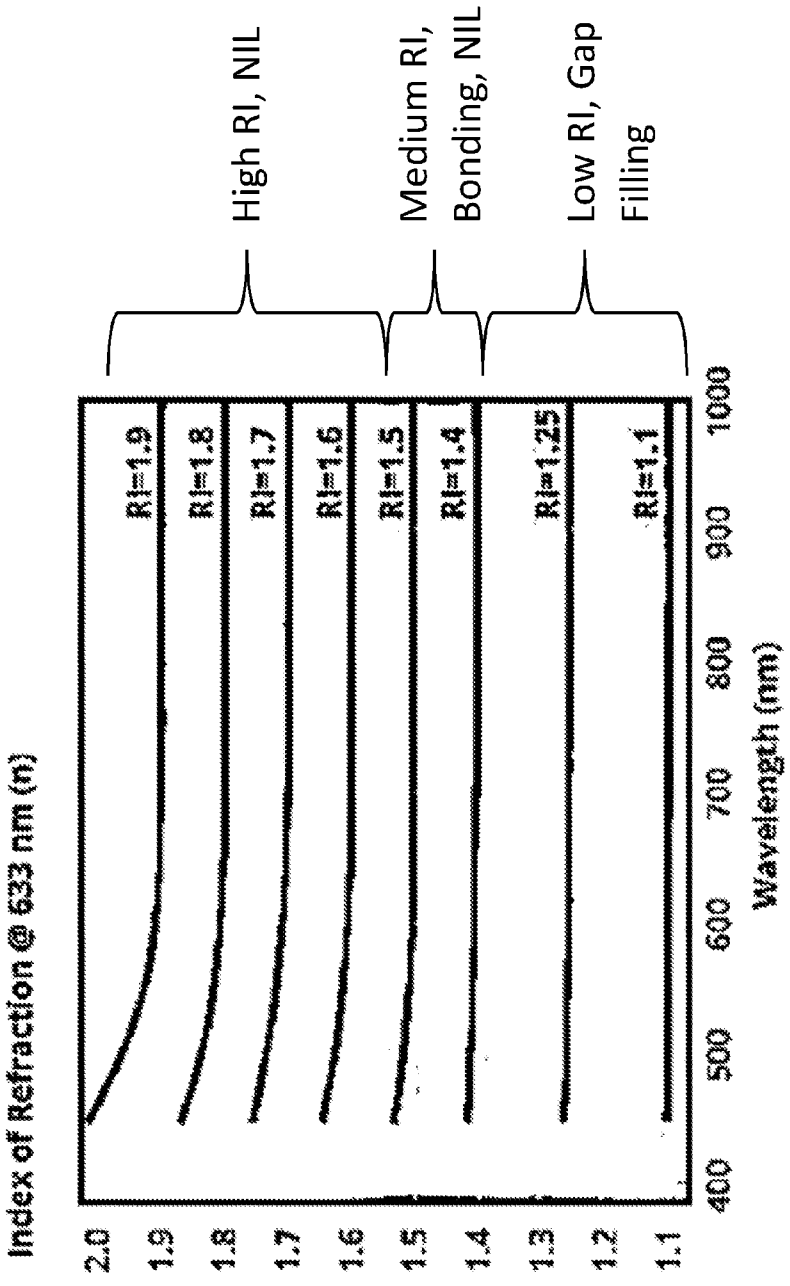
wherein each nanoparticle of a plurality of nanoparticles included in the photoresist has a diameter selected from a range from 10 nm to 20 nm such that the photoresist is ultra-violet curable.

FIG. 1A



PRIOR ART

FIG. 1B



PRIOR ART

FIG. 2

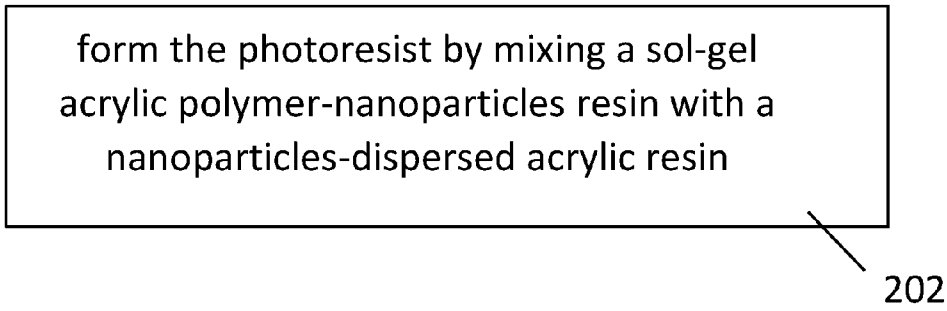

form the photoresist by mixing a sol-gel acrylic polymer-nanoparticles resin with a nanoparticles-dispersed acrylic resin
202

FIG. 3

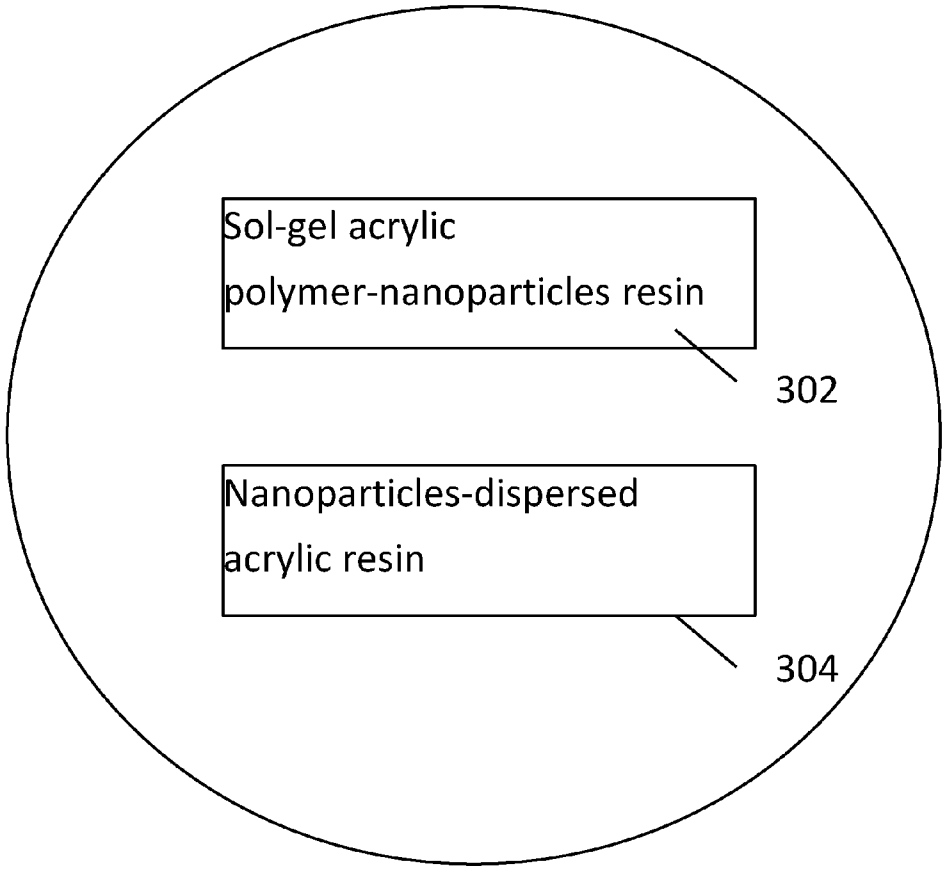

Sol-gel acrylic polymer-nanoparticles resin
302
Nanoparticles-dispersed acrylic resin
304

FIG. 4

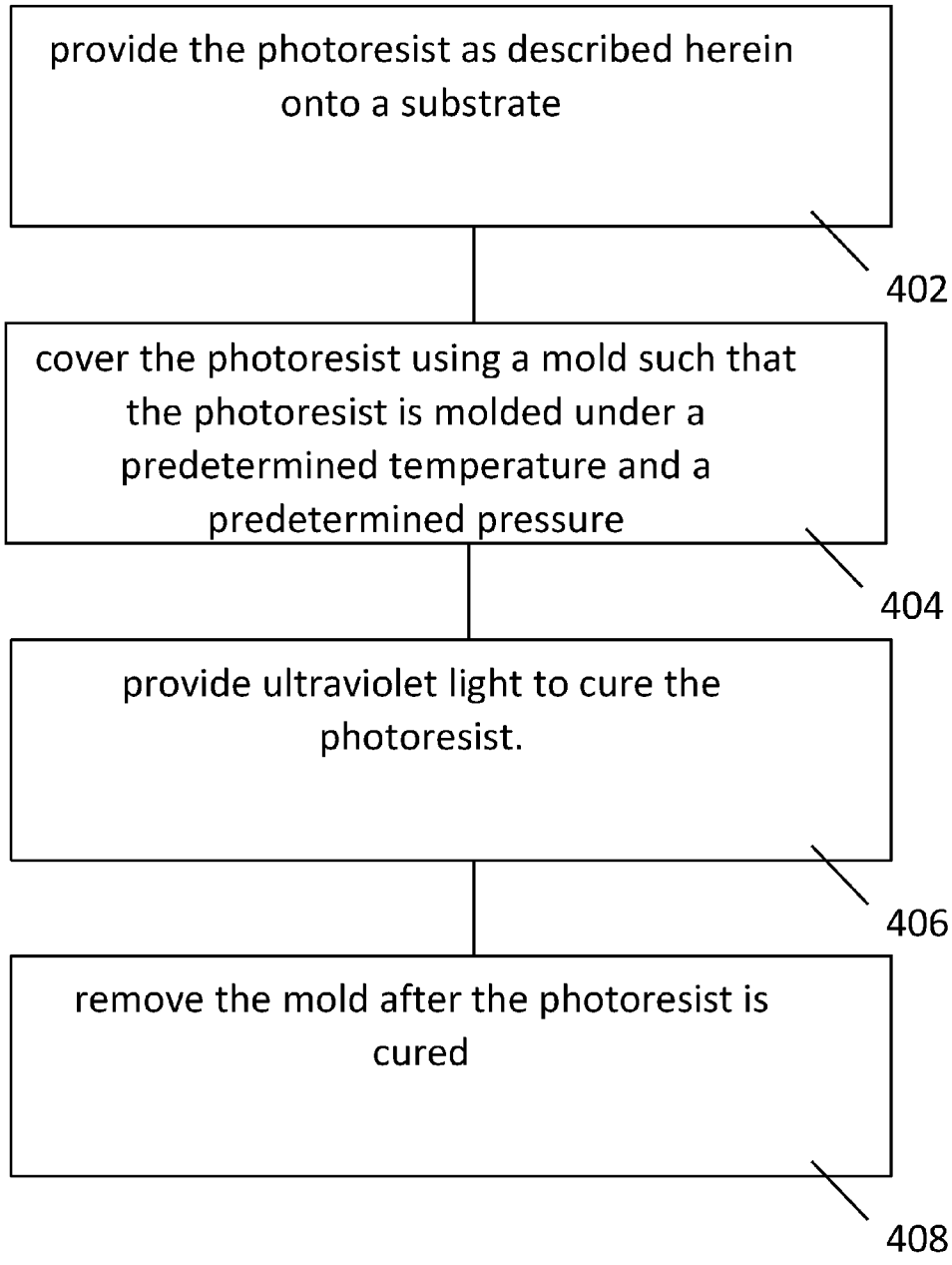

provide the photoresist as described herein onto a substrate
402
cover the photoresist using a mold such that the photoresist is molded under a predetermined temperature and a predetermined pressure
404
provide ultraviolet light to cure the photoresist.
406
remove the mold after the photoresist is cured
408

FIG. 5A

Sample	methyl methacrylate (MMA)	pentabromobenzyl methacrylate (BMA)	titanium isopropoxide (TI)	trimethoxy(7-octen-1-yl)silane (TS)	poly(ethylene glycol dimethacrylate) (PEGD)	dimethoxy phenylacetophenone (DPAP)	temperature	mixing time
PMMA-TiO2-64.6%	0.5 ml	0	3.5 ml	0.5 ml	0.5 ml	50 mg	25 °C	5 hours

FIG. 5B

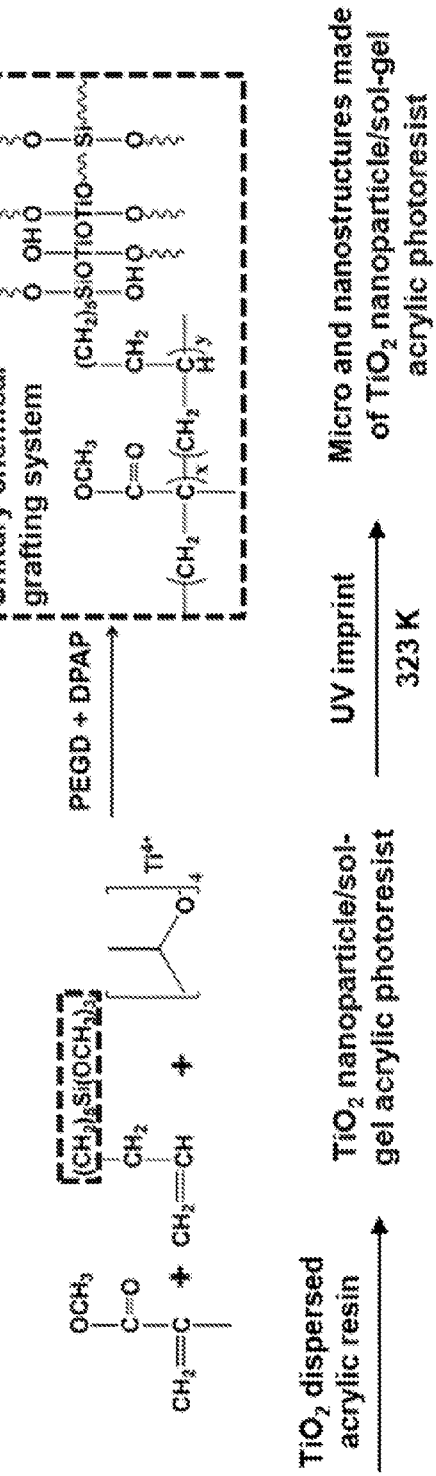

Unitary chemical grafting system
PEGD + DPAP
UV imprint
323 K
Micro and nanostructures made of TiO2 nanoparticle/sol-gel acrylic photoresist
TiO2 dispersed acrylic resin
TiO2 nanoparticle/sol-gel acrylic photoresist

FIG. 6A

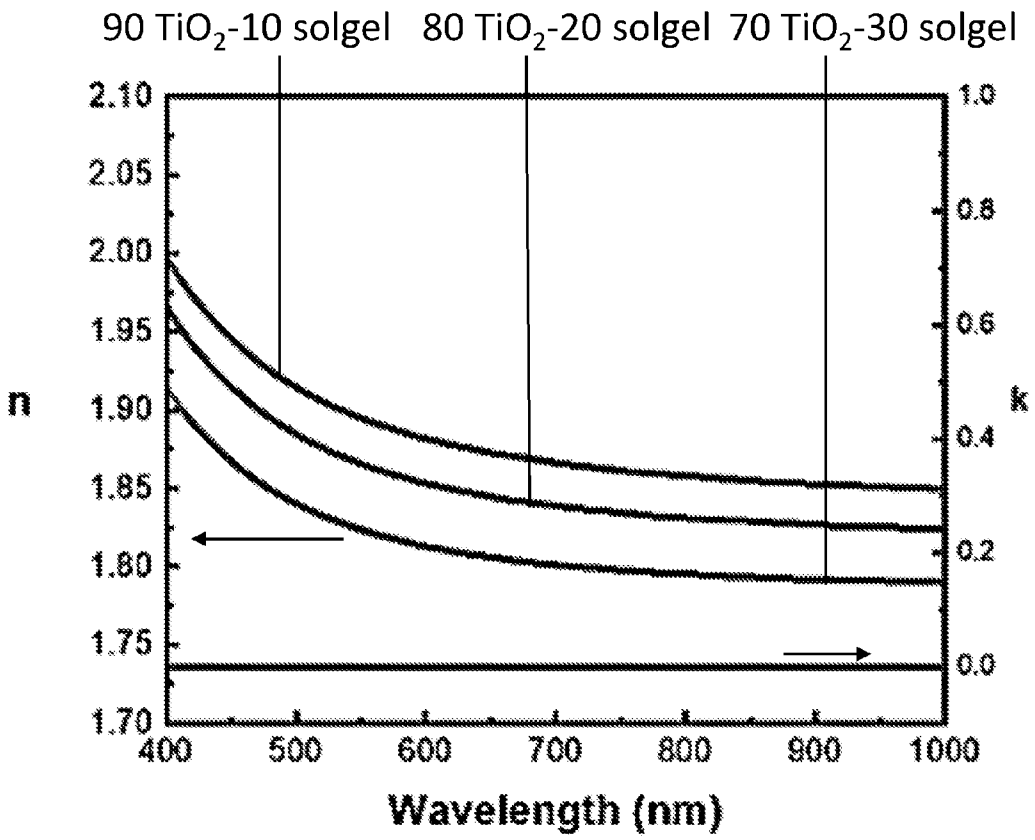

90 TiO2-10 solgel
80 TiO2-20 solgel
70 TiO2-30 solgel
n
k
2.10
2.05
2.00
1.95
1.90
1.85
1.80
1.75
1.70
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
800
900
1000
Wavelength (nm)

FIG. 6B

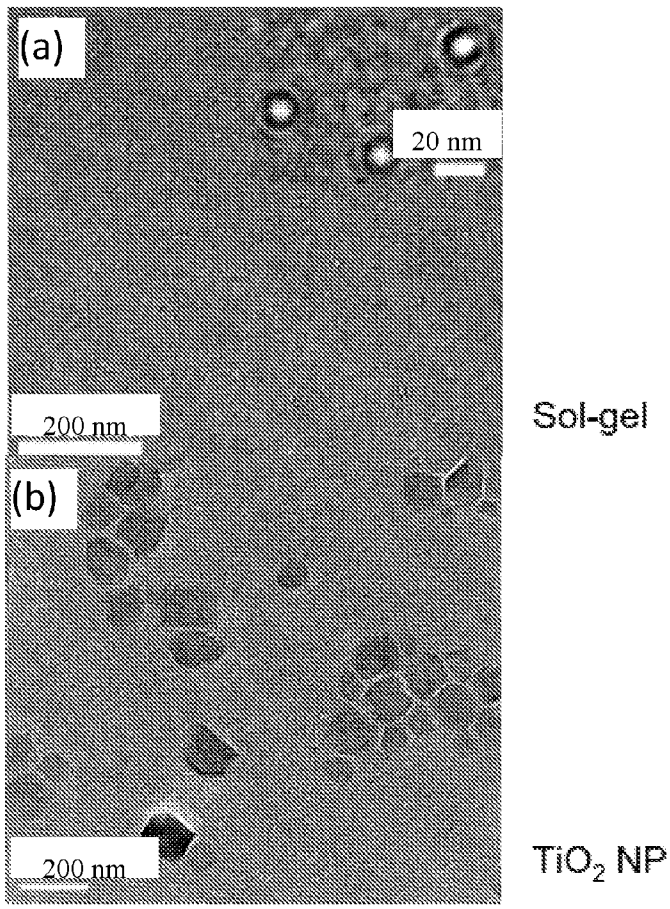


FIG. 7

Nanoimprint stage	Set Pressure	Set Temperature	Thermal Pressing And Holding Time	UV-NIL Exposure Duration	Demold Temperature	UV Wavelength
i	Atm. pressure	50 °C	120 s	N.A.	Room temperature (25 – 30 °C)	365 nm
Ii	Atm. pressure	50 °C	N.A.	6 mins (with 6s 'on' and 6s 'off' cycle)	Room temperature (25 – 30 °C)	365 nm

FIG. 8

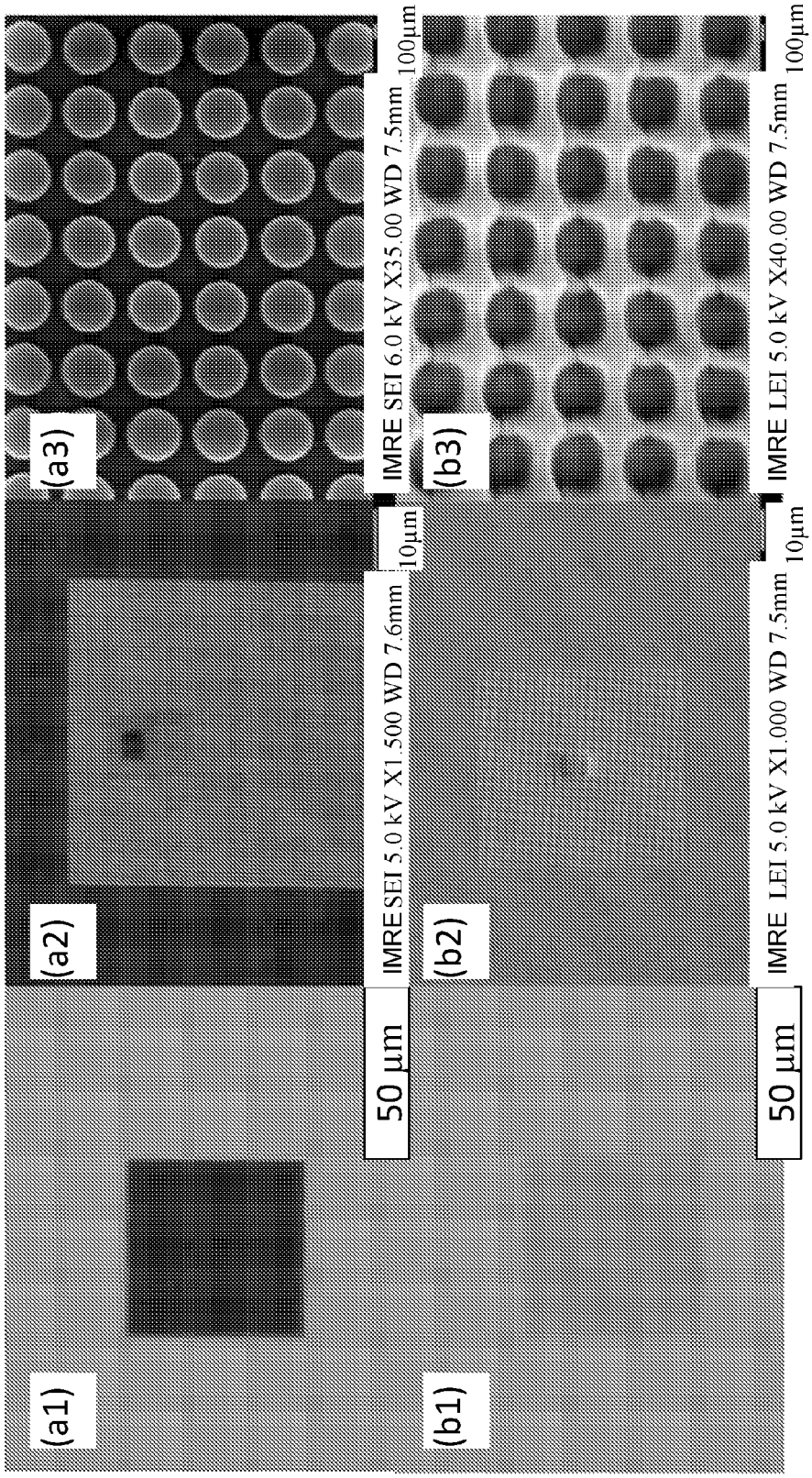

(a1)
(a2)
(a3)
(b1)
(b2)
(b3)
50 µm
IMRE SEI 5.0 kV X1,500 WD 7.6mm
10µm
IMRE SEI 6.0 kV X35.00 WD 7.5mm
100µm
50 µm
IMRE LEI 5.0 kV X1,000 WD 7.5mm
10µm
IMRE LEI 5.0 kV X40.00 WD 7.5mm
100µm

FIG. 9

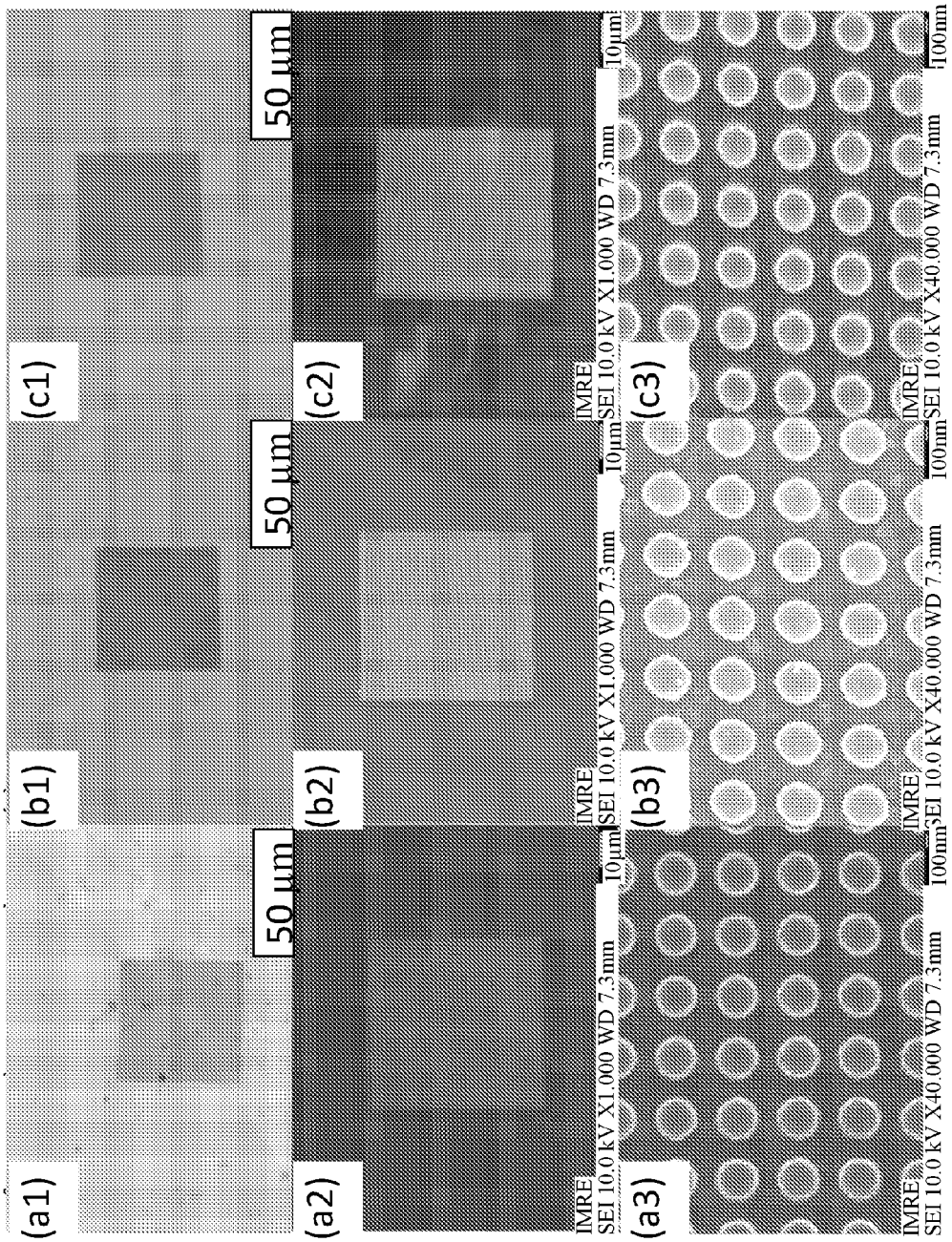

(a1)
(b1)
(c1)
50 µm
(a2)
(b2)
(c2)
50 µm
IMRE
SEI 10.0 kV X1,000 WD 7.3mm
10µm
(a3)
(b3)
(c3)
IMRE
SEI 10.0 kV X40,000 WD 7.3mm
100nm

FIG. 10

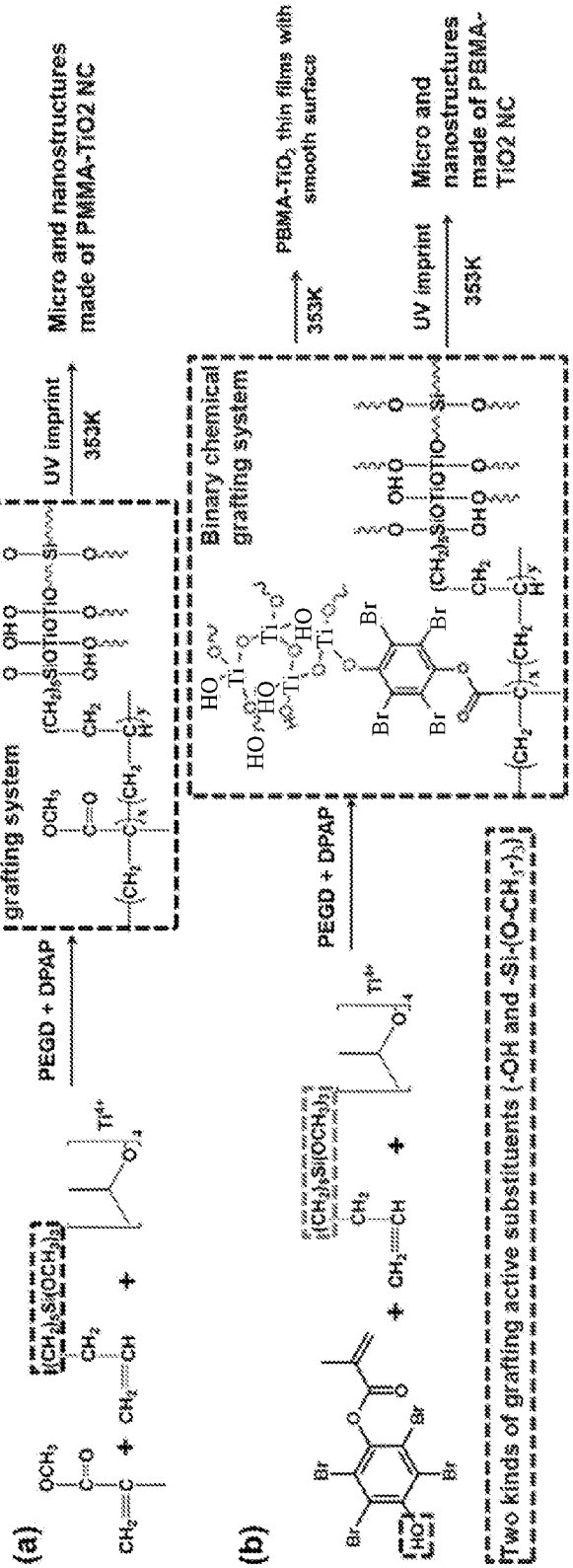

(a)
PEGD + DPAP
Unitary chemical grafting system
353K
PMMA-TiO2 thin films with smooth surface
UV imprint
353K
Micro and nanostructures made of PMMA-TiO2 NC
(b)
PEGD + DPAP
Binary chemical grafting system
353K
PBMA-TiO2 thin films with smooth surface
UV imprint
353K
Micro and nanostructures made of PBMA-TiO2 NC
Two kinds of grafting active substituents (-OH and -Si-(O-CH2-)3)

FIG. 11A

Sample	methyl methacrylate (MMA)	pentabromobenzyl methacrylate (BMA)	titanium isopropoxide (TI)	trimethoxy(7-octen-1-yl)silane (TS)	polyethylene glycol dimethacrylate) (PEGD)	dimethoxy phenylacetophenone (DPAP)	Temperature	Mixing time
PMMA-TiO_2-64.6%	0.5 ml	0	3.5 ml	0.5 ml	0.5 ml	50 mg	25 °C	5 h
PBMA-TiO_2-69.2%	0	0.5 ml	3.5 ml	0.5 ml	0.5 ml	50 mg	25 °C	5 h

FIG. 11B

Nanoimprint stage	Set Pressure	Set Temperature	Thermal NIL holding time	UV exposure duration	Demold temperature	UV Wavelength
i	10 bar	80 °C	120 s	N.A.	Room temperature (25-30 °C)	365 nm
ii	atm pressure	Room temperature (25-30 °C)	N.A.	5 mins (with 5s 'on' and 5s 'off' cycle)	Room temperature (25-30 °C)	365 nm

FIG. 12

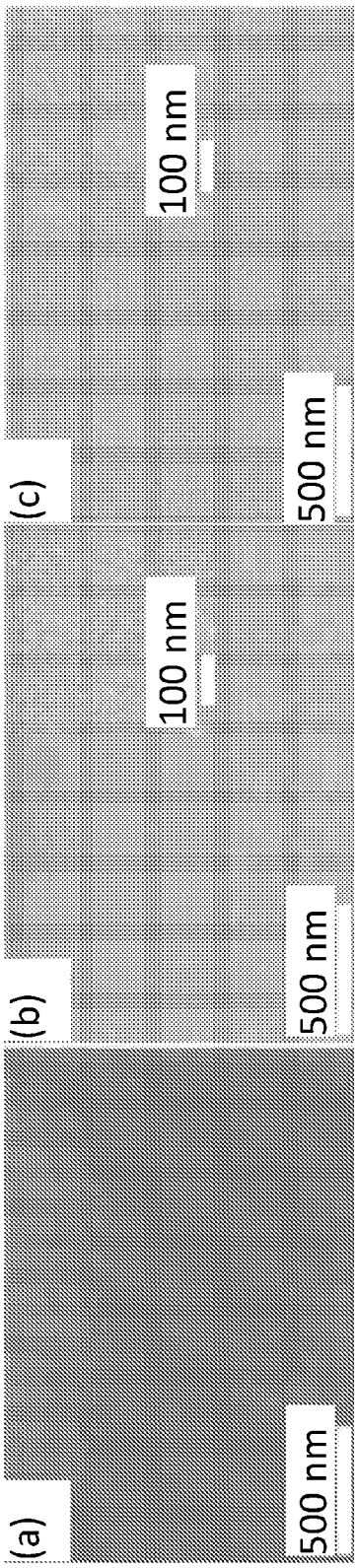


FIG. 13A

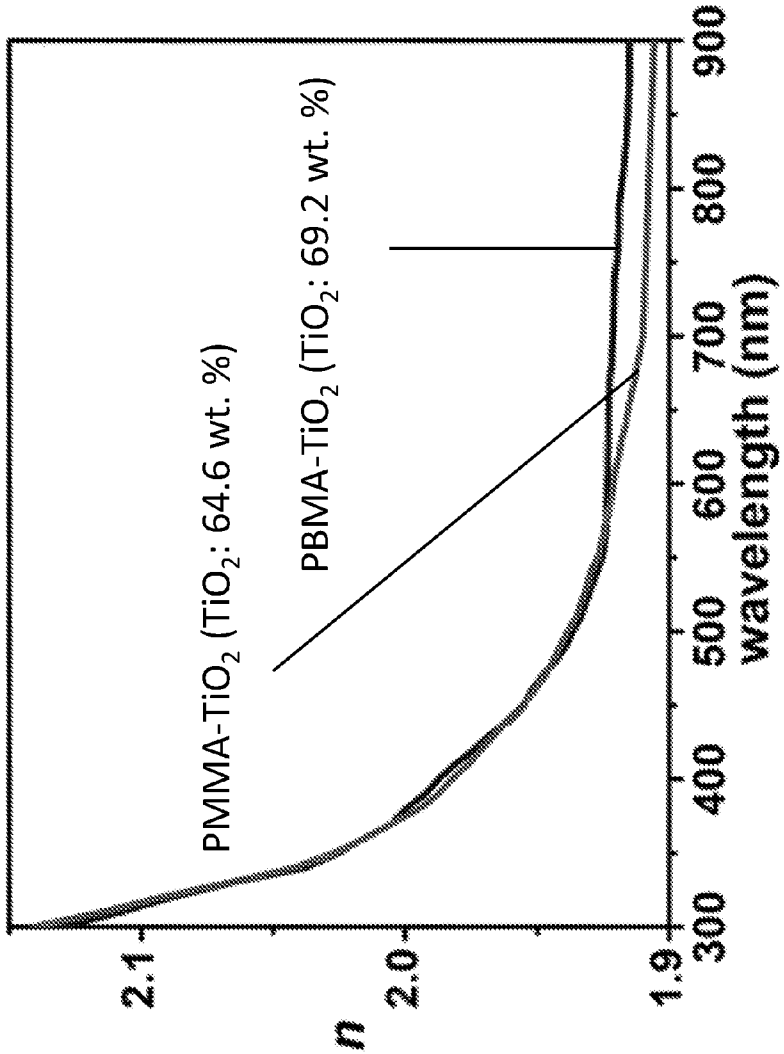

PMMA-TiO2 (TiO2: 64.6 wt. %)
PBMA-TiO2 (TiO2: 69.2 wt. %)
n
2.1
2.0
1.9
300
400
500
600
700
800
900
wavelength (nm)

FIG. 13B

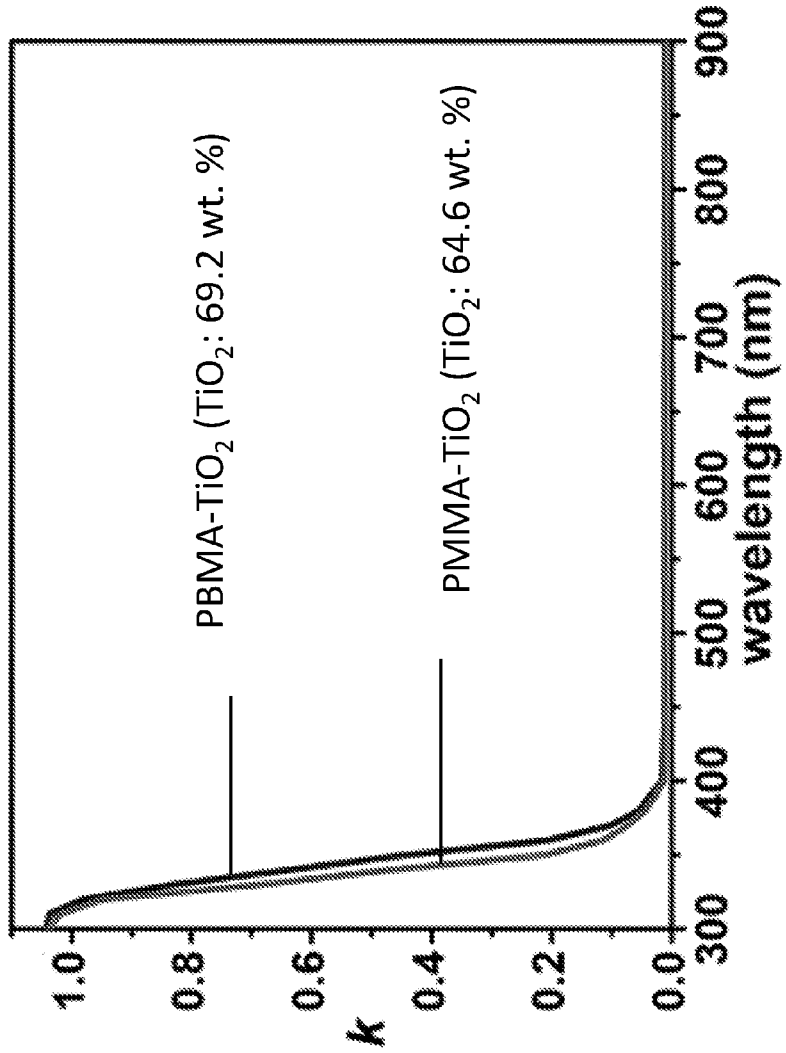

PBMA-TiO2 (TiO2: 69.2 wt. %)
PMMA-TiO2 (TiO2: 64.6 wt. %)
k
wavelength (nm)
1.0
0.8
0.6
0.4
0.2
0.0
300
400
500
600
700
800
900

FIG. 13C

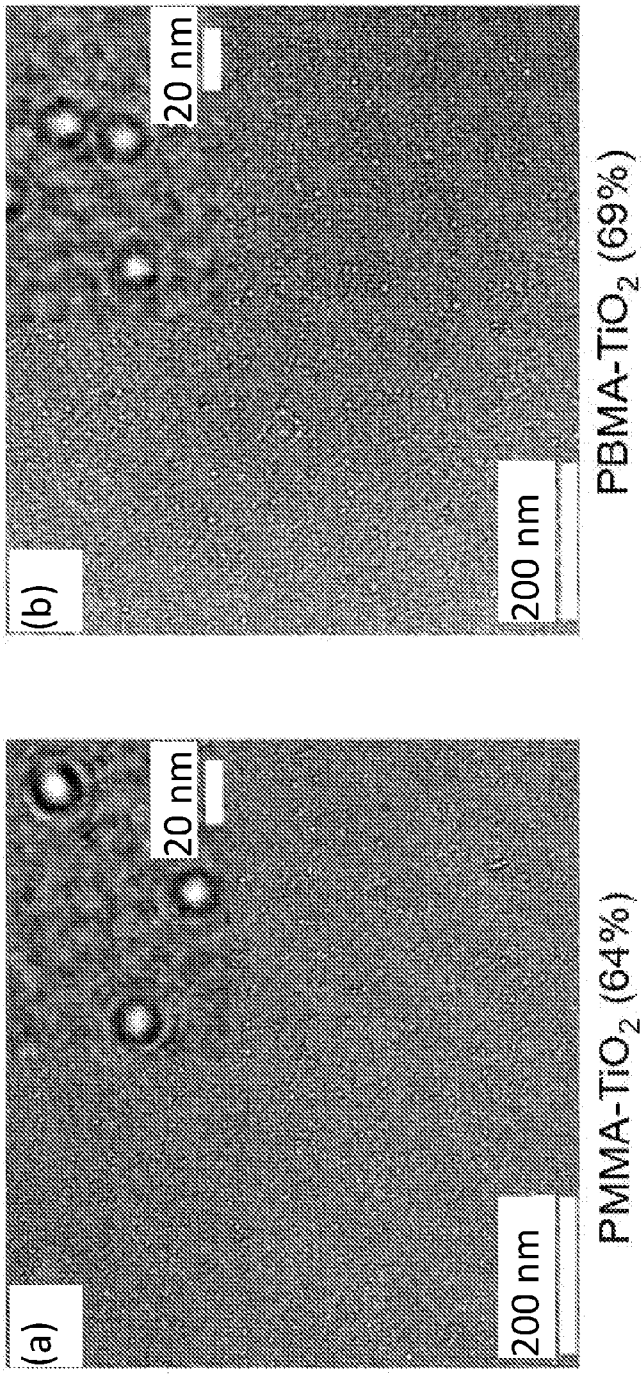


FIG. 14

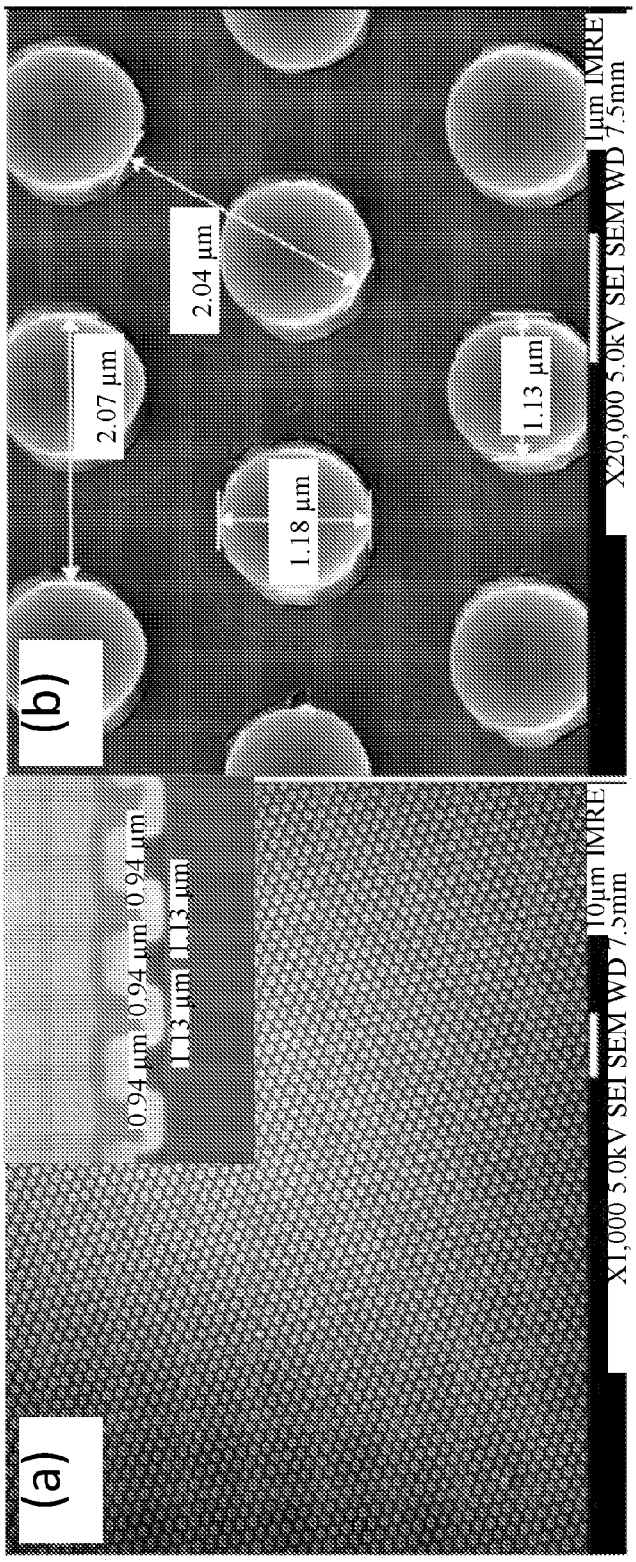

(a)
0.94 µm
0.94 µm
0.94 µm
1.13 µm
1.13 µm
X1,000 5.0kV SEI SEM WD 7.5mm
10µm IMRE
(b)
2.07 µm
2.04 µm
1.18 µm
1.13 µm
X20,000 5.0kV SEI SEM WD 7.5mm
1µm IMRE

FIG. 15

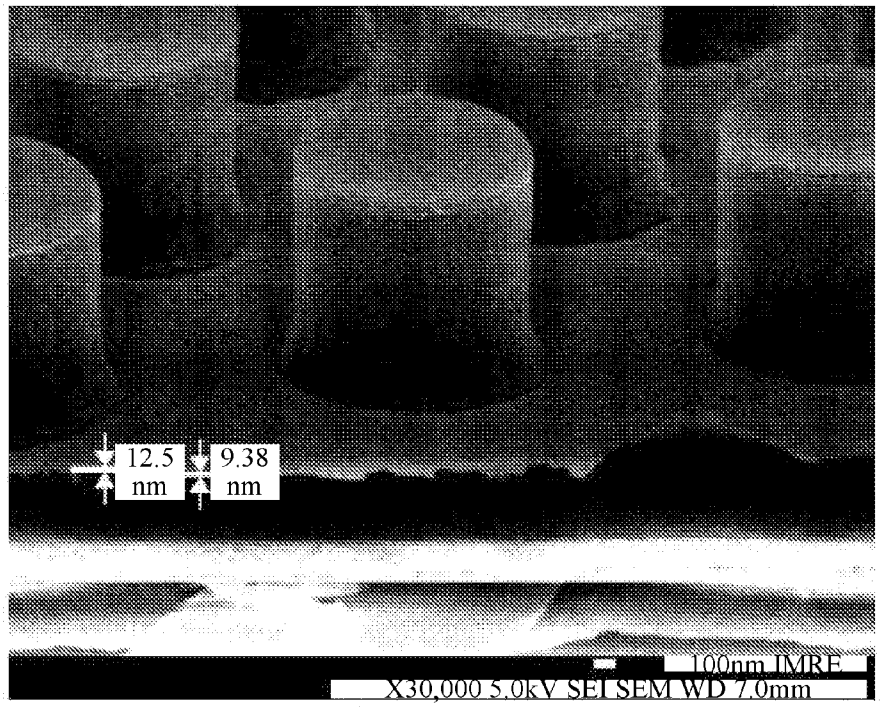


FIG. 16

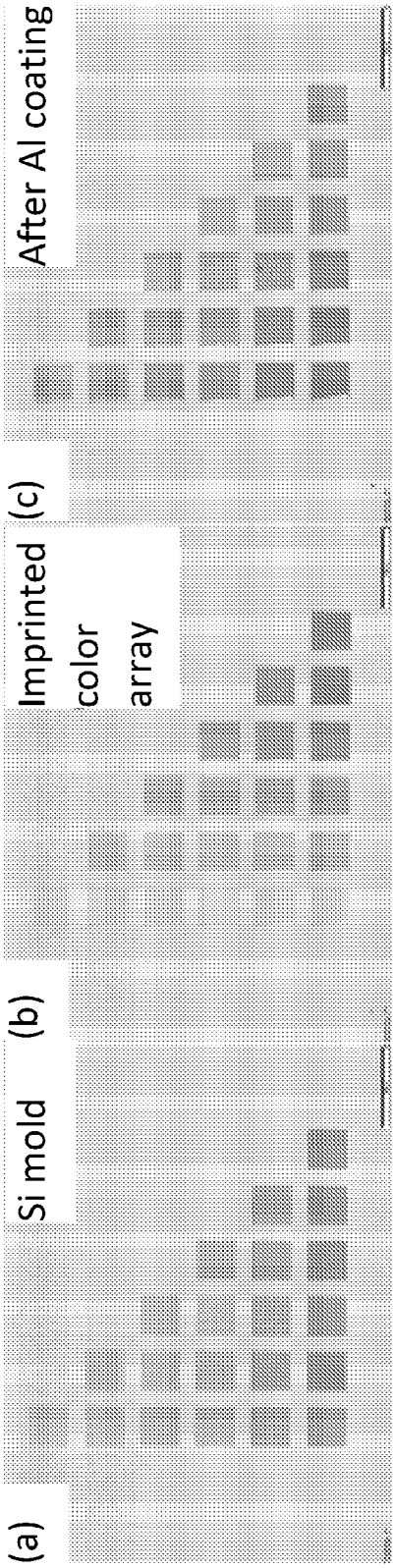


FIG. 17

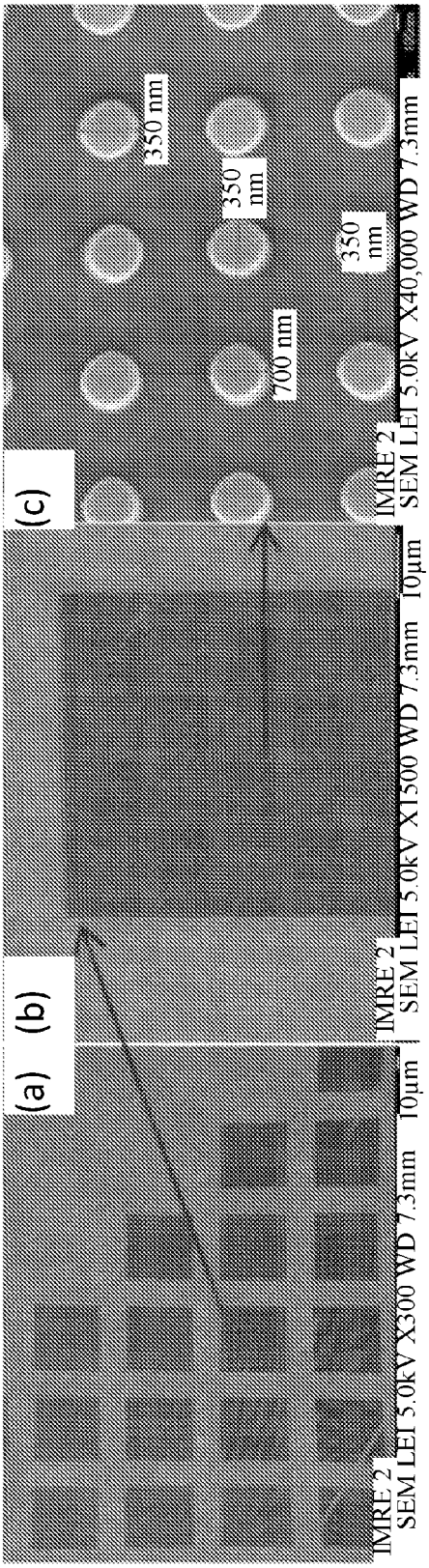

(a)
(b)
(c)
350 nm
350 nm
350 nm
700 nm
IMRE 2
SEM LEI 5.0kV X300 WD 7.3mm 10µm
IMRE 2
SEM LEI 5.0kV X1500 WD 7.3mm 10µm
IMRE 2
SEM LEI 5.0kV X40,000 WD 7.3mm

FIG. 18

Property	**Embodiment**	**Conventional resist 1**	**Conventional resist 2**	**Conventional resist 3**
Refraction index at 589 nm	1.93	1.85	1.57	1.94
Thickness at 1000 rpm	0.5 μm	0.5 μm	10 – 100 μm	-
Transmittance 420 nm	> 80%	> 95%	> 80%	> 63%
Imprint quality	High fidelity of pattern transfer	-	-	Non-uniformity
Solvent	Not required	Required	Required	Required (methyl isobutyl ketone)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2024/050353

A. CLASSIFICATION OF SUBJECT MATTER

See Supplemental Box

According to International Patent Classification (IPC)

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

G03F

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

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

Databases: FAMPAT, CAplus, INSPEC, COMPENDEX and SCISEARCH
Keywords: sol-gel, acrylate, inorganic particle, titania, dispersion, nanocomposite, and related terms.

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	CN 101423678 A (NATIONAL CENTER FOR NANOSCIENCE AND TECHNOLOGY CHINA) 6 May 2009 see whole document, particularly, abstract, paragraphs [0051]-[0061], [0066] and [0095], Tables 5-7, Embodiments 9-14 and Fig. 1 of the machine translation	15-20 1-14
X A	ZHANG, X. ET AL., Stabilized dispersions of titania nanoparticles via a sol–gel process and applications in UV-curable hybrid systems. *Polymer International*, 7 March 2006, Vol. 55, No. 4, pages 466-472 [Retrieved on 2024-08-29] <DOI: 10.1002/PI.2000> see whole document, particularly, abstract, EXPERIMENTAL, page 469, right column, 3rd paragraph and page 470, left column, 1st paragraph, scheme 1, and Figs. 4 and 6	15-20 1-14
A	LEE, L.H. ET AL., High-Refractive-Index Thin Films Prepared from Trialkoxysilane-Capped Poly(methyl methacrylate)-Titania Materials. *Chemistry of Materials*, 17 February 2001, Vol. 13, No. 3, pages 1137-1142 [Retrieved on 2024-08-28] <DOI: 10.1021/CM000937Z> see whole document	1-20

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

*Special categories of cited documents:

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

"D" document cited by the applicant in the international application

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

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

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

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

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

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

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

"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
29/08/2024 *(day/month/year)*	06/09/2024 *(day/month/year)*

Name and mailing address of the ISA/SG	Authorized officer
Intellectual Property Office of Singapore 1 Paya Lebar Link, #11-03 PLQ 1, Paya Lebar Quarter Singapore 408533	Joan Toh (Dr)
Email: pct@ipos.gov.sg	IPOS Customer Service Tel. No.: (+65) 6339 8616

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2024/050353

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	YOON, G. ET AL., Single-step manufacturing of hierarchical dielectric metalens in the visible. *Nature Communications*, 8 May 2020, Vol. 11, No. 1, pages 2268 (1-10) [Retrieved on 2024-08-29] <DOI: 10.1038/S41467-020-16136-5> see whole document	1-20
A	WO 2022/204586 A1 (PIXELLIGENT TECH LLC) 29 September 2022 & US 2024/0191056 A1 see whole document of the patent family member	1-20

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2024/050353

Supplemental Box
(Classification of Subject Matter)

Int. Cl.
G03F 7/00 (2006.01)
G03F 7/004 (2006.01)
C08L 33/12 (2006.01)
C08L 33/16 (2006.01)
C08K 3/22 (2006.01)

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/SG2024/050353

Note: This Annex lists known patent family members relating to the patent documents cited in this International Search Report. This Authority is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
CN 101423678 A	06/05/2009	NONE	
WO 2022/204586 A1	29/09/2022	CN 117916299 A	19/04/2024
		KR 20230162647 A	28/11/2023
		JP 2024-514459 A	02/04/2024
		EP 4314146 A1	07/02/2024
		US 2024/0191056 A1	13/06/2024