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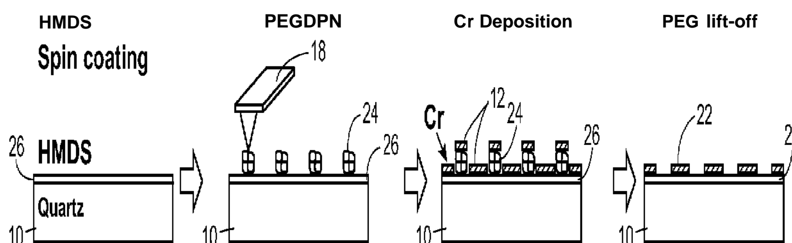

FIG, 1C

(57) Abstract: A method of forming a photomask using a microtip is disclosed herein. The method can include depositing a sacrificial pattern on a substrate using a microtip, forming a mask layer over the sacrificial pattern, and removing the sacrificial pattern and a portion of the mask layer disposed on the sacrificial pattern to form a photomask.

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GENERATION OF PHOTOMASKS BY DIP-PEN NANOLITHOGRAPHY

CROSS-REFERENCE TO RELATED APPLICATION

[0001] The benefit under 35 U.S.C. § 119(e) of U.S. Provisional Patent Application No. 61/055,055 filed May 21, 2008, the disclosure of which is incorporated herein by reference, is hereby claimed.

STATEMENT OF GOVERNMENTAL INTEREST

[0002] This invention was made with government support under grant no. EEC-0647560 awarded by the National Science Foundation-Nanoscale Science and Engineering Center (NSF/NSEC) and under grant no. FA9550-08-1-0124 awarded by Air Force Office of Science Research (AFOSR). The government has certain rights in the invention.

BACKGROUND

Field of the Disclosure

[0003] The disclosure generally relates to dip-pen nanolithography generated photomasks. In particular, this disclosure relates to dip-pen nanolithography generated photomasks, and their use in fabrication of electrodes for the electrical measurement of nanomaterials.

Background of Related Technology

[0004] Dip-pen nanolithography (DPN) is an effective and powerful nanofabrication tool for a wide variety of metal and semiconductor substrates with many types of deposition materials, including small organic molecules, polymers, DNA, proteins, peptides, metal ions, and nanoparticles. The hard resolution and materials flexibility of DPN make it particularly attractive for many applications in the life sciences and semiconductor industries. DPN has been used to prepare gene chips and proteomic arrays for applications ranging from biodiagnostics to studies of cell-surface interactions.

[0005] In recent years, DPN has been transformed from a serial to a massively parallel process capable of using as many as 55,000 AFM cantilevers to print nanostructures and for negative tone nanostructure fabrication using a DPN pattern as a sacrificial material.

SUMMARY

[0006] A method of forming a photomask includes depositing a sacrificial pattern on a substrate using a microtip or a microstamp, forming a mask layer over the sacrificial pattern, and removing the sacrificial pattern and the portion of the mask layer disposed on the sacrificial pattern, to form a photomask.

[0007] Another method of forming a photomask includes depositing a resist pattern over a mask layer using a microtip or microstamp, the mask layer disposed over a substrate, and patterning the mask layer using the resist pattern as a mask to form a photomask.

[0008] Another method of forming a photomask includes depositing a sacrificial pattern over a mask layer using a microtip or microstamp, the mask layer being disposed over a substrate, depositing a resist material over the combination of mask layer and sacrificial pattern, wherein the resist material selectively forms on the mask layer between adjacent elements of the sacrificial pattern, thereby forming a resist pattern, removing the sacrificial pattern, and patterning the mask layer using the resist pattern as a mask to form a photomask.

[0009] A method of forming an electrode includes patterning an electrode substrate using a photomask described herein, by a method described herein, to form an electrode.

BRIEF DESCRIPTION OF THE DRAWINGS

[0010] Figures IA- 1C are schematics of a photomask fabrication process in accordance with embodiments of the disclosed invention.

[0011] Figure 2A is an image of a Cr positive tone photomask formed by a method in accordance with an embodiment of the disclosed invention. Figure 2B is an optical microscopy image of the critical region of a Cr photomask formed by a method in accordance with an embodiment of the disclosed invention. The inset of Figure 2B is an optical microscopy image of a one-dimensional cantilever array employed for DPN. Figure 2C is an optical microscopy image of a Au electrode formed using the photomask of Figure 2B. Figure 2D is a scanning electrode microscopy (SEM) image of the electrode of Figure 2C connected to a current-voltage meter. Figure 2E is a graph of an I-V curve of polypyrrole (PPy) nanotubes drop cast on the electrode of Figure 2D, measured with and without UV irradiation. The inset image of Figure 2E is an optical microscopy image of PPy nanotubes loaded on the electrode of Figure 2D.

[0012] Figures 3A and 3B are images illustrating a comparison between photomask design and resulting photomask structure formed in accordance with the method illustrated in Figure IB. Figure 3A is images of a pattern design for a positive type photomask and the resulting photomask. Figure 3B is images of a pattern design for a negative type photomask and the resulting photomask.

[0013] Figure 4A is an optical microscopy image of a Cr negative tone photomask formed by a method in accordance with an embodiment of the disclosed invention. Figure 4B is a

SEM image of the critical region of a Cr photomask formed by a method in accordance with an embodiment of the disclosed invention. Figure 4C is an optical microscopy image of an electronic device formed using the photomask of Figure 4B and connected to electrode leads. Figure 4D is a graph of an I-V curve of PPy nanowire disposed beneath the electrode of Figure 4C, measured with and without UV irradiation.

[0014] Figure 5A is an optical microscopy image of a 3 x 3 PEG dot array pattern on HMDS spin-coated quartz. Figure 5B is a tapping mode 3-D atomic force microscopy image of the PEG dot array of Figure 5A. Figure 5C is an optical microscopy image of a negative tone Cr photomask formed from the PEG dot array of Figure 5A by a lift-off process in accordance with an embodiment of the disclosed invention. Figure 5D is a 3 x 3 Au dot array pattern formed using the photomask of Figure 5C.

[0015] Figure 6A is an optical microscopy image of an electrode array design having an electrode formed using a photomask formed by a method in accordance with an embodiment of the disclosed invention. Figure 6B is an optical microscopy image of the electrode array of Figure 6A, before formation of electrode leads. Figure 6C is an optical microscopy image of an entire electrode array having electrodes formed using a photomask formed by a method in accordance with an embodiment of the disclosed invention and connected to electrode leads. Figure 6D is an SEM image of the electrode array of Figure 6C.

[0016] Figure 7A is a schematic illustrating a method of forming a bottom electrode using a photomask formed by a method in accordance with an embodiment of the disclosed invention. Figure 7B s a schematic illustrating a method of forming a top electrode using a photomask formed by a method in accordance with an embodiment of the disclosed invention.

[0017] Figures 8A and 8B are SEM images of PPy nanotubes used in the measurements reported in Figure 2E. Figures 8C and 8D are SEM images of PPy nanowires used in the measurements reported in Figure 4D.

[0018] Figure 9A is a graph illustrating the height as function of the full width at half maximum for PEG DPN dots patterned on HMDS-coated quartz. Figure 9B is a graph illustrating the relationship between dot feature size and tip dwell time of PEG DPN dots patterned on HMDS-coated quartz.

DETAILED DESCRIPTION

[0019] A photomask can include a mask pattern disposed on a substrate. Photomasks can be positive or negative. Each of the methods described herein can be used to form both positive- and negative-type photomasks.

[0020] Referring to Figure IA, in accordance with an embodiment of the invention, a method of forming a photomask can include forming a mask layer 12 over a substrate 10 and forming a resist pattern 16 over the mask layer 12 using a microtip 18. The mask layer 12 can then be patterned, e.g. by etching, using the resist pattern 16 as an etching resist mask to form a mask pattern 22. The method can further include removing the resist pattern 16 from the mask pattern 22, such that only the mask pattern 22 remains on the substrate 10.

[0021] Optionally, the method can include forming a supplemental resist layer 14 over the mask layer 12. The resist pattern 16 can be formed over the supplemental resist layer 14 using the microtip 18. The supplemental resist layer 14 can then be patterned, e.g. by etching, using the resist pattern 16 as an etching mask to form a supplemental resist pattern 20. The mask layer 12 can be patterned, e.g. by etching, using, for example, one or both of the supplemental resist pattern 20 and the resist pattern 16 to form the mask pattern 22. The resist pattern 16 and the supplemental resist pattern 20 can be removed, such that only the mask pattern 22 remains on the substrate 10.

[0022] Referring to Figure IB, in accordance with another embodiment of the invention, a method of forming a photomask can include forming a mask layer 12 over a substrate 10 and depositing a sacrificial pattern 24 over the mask layer 12 using a microtip 18. A resist material can then be formed over the sacrificial pattern. The resist material selectively forms on the mask layer 12 between adjacent elements of the sacrificial pattern 24. The sacrificial pattern 24 can then be removed, leaving the resist pattern 16 on the mask layer 12. The mask layer 12 can be patterned, e.g. by etching, using the resist pattern 16 as an etching mask to form a mask pattern 22. The resist pattern 16 can then be removed, thereby leaving the mask pattern 22 on the substrate 10 to form the photomask.

[0023] The method can further include forming a supplemental resist layer 14 over the mask layer 12. The resist pattern 16 can be formed over the supplemental resist layer 14 using a microtip 18. The supplemental resist layer 14 can then be patterned, e.g. by etching, using the resist pattern 16 as an etching mask to form a supplemental resist pattern 20. The mask layer 12 can be patterned using, for example, one or both of the supplemental resist

pattern 20 and the resist pattern 16 to form a mask pattern 22. The resist pattern 16 and the supplemental resist pattern 20 can be removed, such that only the mask pattern 22 remains on the substrate 10.

[0024] Referring to Figure 1C, in accordance with yet another embodiment of the invention, a method of forming a photomask can include forming a sacrificial pattern 24 over a substrate 10 using a microtip 18 and forming a mask layer 12 over the sacrificial pattern 24. The sacrificial pattern 24 and the portion of the mask layer 12 disposed over the sacrificial pattern 24 are removed, for example using a lift-off process, thereby forming a mask pattern 22 and the photomask. Preferably, the thickness of the sacrificial pattern 24 is greater than the thickness of the mask layer 12.

[0025] The method can further including forming an adhesion layer 26 over the substrate 10 before forming the sacrificial pattern 24. The adhesion layer 26 can be, for example, an HDMS layer. Other suitable adhesion layers include, for example, amino propyl trimethoxyl silane (APTMS), polydimethylsiloxane (PDMS), and mercapto propyl trimethoxyl silane (MPTMS). The adhesion layer 26 can have a thickness, for example, in a range of about 1 nm to 500 nm. Other suitable thicknesses include from about 5 to 400 nm, 20 nm to 300 nm, about 30 nm to 200 nm, about 40 nm to 100 nm, and about 50 nm to about 75 nm. The thickness can be, for example, about 1, 2, 3, 4, 5, 5, 6, 7, 8, 9, 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 250, 300, 350, 400, 450, or 500 nm. The adhesion layer 26 can be formed on the substrate 10 by spin coating, for example. Any other suitable method can be used for forming the adhesion layer 26.

Substrate

[0026] The substrate 10 can be, for example, a transparent substrate 10, such as glass, for example, quartz glass. Other suitable substrate materials include, for example, CaF_2, mica, plastic, polymethyl methacrylate (PMMA), polypropylene, indium tin oxide (ITO), and polystyrene (PS). The substrate 10 can have a thickness in a range of 1 µm to 5000 µm. Other suitable thickness include from about 1 µm to 10 µm, 50 µm to 2500 µm, 150 µm to 1000 µm, 300 µm to 800 µm, and 400 µm to 600 µm. Other suitable thicknesses include about 1, 2, 3, 4, 5, 6, 7, 8, 9, 10, 20 , 30, 40, 50, 60 ,70 , 80, 90, 100, 150, 200, 250, 300, 350, 400 ,450, 500 ,550, 600, 650, 700, 750, 800, 850, 900, 950, 1000, 1500, 2000, 2500, 3000, 3500, 4000, 4500, and 5000 µm.

Mask Layer

[0027] The mask layer 12 preferably comprises or consists of an inorganic material, preferably a metal or metal oxide. For example, the mask layer 12 can be formed from Cr, CrN, Mo, Nb_2O_5, Ti, Ta, CrN, MoO_3, MoN, Cr_2O_3, TiN, ZrN, TiO_2, TaN, Ta_2O_5, SiO_2, NbN, Si_3N_4, ZrN, Al_2O_3N, Al_2O_3R, and combinations thereof. The mask layer 12 can be formed to a thickness in a range of 50 nm to 500 nm. Other suitable thicknesses include from 60 nm to 400 nm, 70 nm to 300 nm, 80 nm to 200 nm, and 90 nm to 100 nm. The mask layer 12 can be formed to a thickness, for example, of about 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 225, 250, 275, 300, 325, 350, 375, 400, 425, 450, 475, or 500 nm. The mask layer 12 can be formed on the substrate 10 using any known methods, including, for example, thermal evaporation, sputtering, and e-beam evaporation.

Resist Pattern

[0028] The resist pattern 16 can be formed from any suitable resist material, and preferably comprises or consists of an organic material, such as alkyl thiols. Suitable organic resist materials include, for example, 1-octadecanethiol (ODT), 1-hexadecanethiol (HDT), 1-dodecanethiol (DDT), 11-mercaptoundecanoic acid (MUA), ferrocenyl undecanethiol and 16-mercaptohexadecanoic acid (MHA). The resist pattern 16 can be formed, for example, of self-assembled monolayers of ODT. The resist material can be coated on a microtip 18 or an array of microtips and patterned directly onto a surface, for example, the mask layer 12. Suitable microtips include, for example, atomic force microscopy tip, a scanning microscopy tips, solid tips, hollow tips, or nanoscopic tips. For example, the resist pattern 16 can be formed using direct-write patterning methods, such as dip-pen nanolithography. Referring to Figures 9A and 9B, typically, in tip based synthesis methods, such as DPN, the thickness and area of a deposited feature are a function of the tip dwell time.

[0029] The microtip 18 can be coated, for example, with the resist material using thermal evaporation, spin coating, or by dipping the microtip 18 into the resist material. The resist material can be included in a solution, for example, in a solvent, to facilitate coating. The solvent can be evaporated from the resist material upon patterning. Alternatively, the microtip 18 can include a channel or other reservoir to contain the resist material, and the resist material can be dispensed through the channel or a port from the reservoir onto the substrate 10. For example, the microtip can be an evaporator-type tip, in which material disposed in the channel is evaporated from the microtip 18 and onto the substrate 10 by

application of an electric field or temperature gradient. The resist pattern 16 can also be formed using microcontact printing. For example, the resist pattern 16 can be formed by applying the resist material to a microstamp and stamping the resist pattern 16 onto a surface. As another example, an array of resist patterns 16 can be formed using a polymer pen array in a direct writing method using dwell time and contact pressure in order to control feature size.

[0030] Arrays of microtips (cantilevered or non-cantilevered) or microstamps can be used to simultaneously form parts of the resist pattern 16 and/or form multiple resist patterns on multiple surfaces or portions of surfaces. For example, a resist pattern 16 can be formed using an 18-pen one-dimensional cantilever array. The 18-pen array can be formed, for example, from a 26-pen array having 8 of the pens removed to create an array with 16 evenly spaced pens and two additional pens separated from the central 16-pen array. The 16-pen array can be used, for example, to form a resist pattern 16 having parallel lines separated by a gap. Any suitable number of pens in an array can be used, for example, to form the resist pattern 16.

[0031] Deposition of the resist pattern 16 using the microtip 18 can be carried out at various humidity levels. For example, higher humidity such as at least about 40%, at least about 60%, at least about 80%, at least about 90%, and at least about 93% can be used. For example, a 93% humidity and a temperature, for example, of about 28^{0}C can be used for forming the resist pattern 16.

[0032] Referring to Figures 3A and 3B, the resist pattern 16 can have the dimensions of the desired mask pattern 22 to be subsequently formed. For example, the resist pattern 16 can be a pattern of lines and/or dots that are separated by gaps. The lines can be straight or curved. The resist pattern 16 can be formed to have any other suitable pattern elements. For example, the resist pattern 16 can include, for example, a series of parallel lines separated by gaps.

[0033] The lines can have a line width, for example, in a range of 10 nm to 100 μm. Other suitable line widths include, for example, from 20 nm to 80 μm, 40 nm to 60 μm, 80 nm to 40μm, 100 nm to 20 μm, 15 nm to 10 μm, 30 nm to 8 μm, 50 nm to 6 μm, 70 nm to 4 μm, 90 nm to 2 μm, 10 nm to 1 μm, 200 nm to 800 nm, 300 nm to 600 nm, and 400 nm to 500 nm. The line width can be, for example, about 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, 500

nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 950 nm, 1 **μm, 2 μm, 3 μm, 4 μm, 5 μm, 6 μm, 7 μm, 8 μm, 9 μm,** or 100 **μm.**

[0034] The lines can have length, for example, in a range of 10 nm to 1000 μm. Other suitable lengths include, for example, from 20 nm to 800 nm, 40 nm to 600 nm, 60 nm to 400 nm, 80 nm to 200 nm, 90 nm to 150 nm, 100 nm to 1 μm, 500 nm to 5 μm, 700 nm to 50 μm, 20 nm to 100 μm , 50 nm to 500 μm, 70 nm to 800 μm, 5 μm to 900 μm, 10 μm to 800 μm, 20 μm to 700 μm, 30 μm to 600 μm, 40 μm to 500 μm, 50 μm to 400 μm, 60 μm to 300 μm, 70 μm to 200 μm, and 80 μm to 100 μm. The length can be, for example, about 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 950 nm, 1 μm, 10 μm, 20 μm, 30 μm, 40 μm, 50 μm, 60 μm, 70 μm, 80 μm, 90 μm, 100 μm, 150 μm, 200 μm, 250 μm, 300 μm, 350 μm, 400 μm, 450 μm, 500 μm, 550 μm, 600 μm, 650 μm, 700 μm, 750 μm, 800 μm, 850 μm, 900 μm, 950 μm, or 1000 μm.

[0035] The pattern elements can be separated by a gap having a width, for example, in a range of 10 nm to hundreds of micrometer. Suitable gap widths include, for example, from 50 nm to 5 μm, from 100 nm to 1 μm, 200 nm to 800 nm, 300 nm to 600 nm, 400 nm to 500 nm, 100 nm to 100 μm, 150 nm to 200 μm, 200 nm to 500 μm, 300 nm to 700 μm, and 400 nm to 900 μm. The gap width can be, for example, about 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 950 nm, 1 μm, 2 μm, 3 μm, 4 μm, 5 μm, 6 μm, 7 μm, 8 μm, 9 μm, 10 μm, 50μm, 100 μm, 150 μm, 200 μm, 250 μm, 300 μm, 350 μm, 400 μm, 450 μm, 500 μm, 550 μm, 600 μm, 650 μm, 700 μm, 750 μm, 800 μm, 850 μm, 900 μm, or 950 μm.

Supplemental Resist Layer

[0036] The supplemental resist layer 14 can be, for example, gold, silver, aluminum, titanium, and palladium. The supplemental resist layer 14 can be included to allow for smooth and uniform formation of the resist pattern 16 using a microtip 18. For example, when forming the resist pattern 16 using DPN, a gold layer can be formed on the mask layer 12. Gold is compatible with the DPN method and resist materials described herein, allowing for smooth and uniform writing using the tip. It can be difficult to form a pattern using tip-based synthesis such as DPN on mask layers such as chromium. Accordingly, the

supplemental resist layer 14 can be used to facilitate patterning of the resist pattern 16 using the microtip 18.

[0037] The supplemental resist layer 14 can have a thickness, for example, in a range of 10 nm to 1000 nm. Other suitable thicknesses include from about 20 nm to 900 nm, 40 nm to 800 nm, 60 nm to 600 nm, 80 nm to 400 nm, 100 nm to 200 nm, 20 nm to 100 nm, 30 nm to 80 nm, and 40 nm to 60nm. The thickness can be, for example, about 10, 20, 30, 40, 50, 60, 70, 80, 90, 100, 110, 120, 130, 140, 150, 160, 170, 180, 190, 200, 250, 300, 350, 400, 450, 500, 550, 600, 650, 700, 750, 800, 850, 900, 950, or 1000 nm.

Sacrificial Pattern

[0038] The sacrificial pattern 24 can be formed, for example, from an oligomer, a polymer, and combinations thereof. The oligomer or polymer can contain a heteroatom, such as, for example, an oxygen atom or a nitrogen atom. For example, the sacrificial pattern 24 can be formed from poly(ethylene glycol) (PEG) and polypropylene glycol (PPG). The sacrificial pattern 24 can be formed, for example, from a polyether, such as polyalkylene oxides and polyalkylene glycols. The oligomer or polymer can have a melting point, for example, below about 60^0C, such that in higher humidity the material flows well off of a microtip onto a substrate. The oligomer and/or polymer can be water-soluble. Alternatively, the oligomer or polymer can be soluble in an organic solvent, such as, for example, dichloromethane.

[0039] The molecular weight of the oligomer or polymer can be in a range of 100 to 1,000,000. Other suitable molecular weights include, for example, from 200 to 100,000, 500 to 50,000, 1,000 to 10,000, 1,000 to 5,000, and 1,000 to 3,000. For example, the substrate pattern 24 can be formed from PEG having a molecular weight of about 2000. Any other suitable molecular weight oligomers or polymers can be used.

[0040] The sacrificial pattern 24 can have a thickness in range of 10 nm to 10 μm. Other suitable thicknesses include, for example, from 50 nm to 5 μm, from 100 nm to 1 μm, 200 nm to 800 nm, 300 nm to 600 nm, and 400 nm to 500 nm. The line width can be, for example, about 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 950 nm, 1 μm, 2 μm, 3 μm, 4 μm, 5 μm, 6 μm, 7 μm, 8 μm, 9 μm, or 10 μm.

[0041] The sacrificial pattern 24 can be a pattern of lines and/or dots that are separated by gaps. The lines can be straight or curved. The sacrificial pattern 24 can be formed to have

any other suitable pattern elements. For example, the sacrificial pattern 24 can include, for example, a series of parallel lines separated by gaps. The sacrificial pattern 24 can be formed, for example, as a complementary pattern to the mask pattern 22. For example, the lines of a sacrificial pattern 24 can correspond to gaps in a subsequently formed mask pattern 22.

[0042] The sacrificial pattern 24 can have any suitable dimensions based on the desired dimensions of the subsequently formed mask pattern 22. For example, the lines can have a line width, for example, in a range of 10 nm to 100 µm. Other suitable line widths include, for example, from 20 nm to 80 µm, 40 nm to 60 µm, 80 nm to 40 µm, 100 nm to 20 µm, 120 nm to 10 µm, 200 nm to 5 µm, 400 nm to 1 µm, 50 nm to 5 µm, 100 nm to 1 µm, 200 nm to 800 nm, 300 nm to 600 nm, and 400 nm to 500 nm. The line width can be, for example, about 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 950 nm, 1 µm, 2 µm, 3 µm, 4 µm, 5 µm, 6 µm, 7 µm, 8 µm, 9 µm, 10 µm, 20 µm, 30 µm, 40 µm, 50 µm, 60 µm, 70 µm, 80 µm, 90 µm, or 100 µm.

[0043] The lines can have length, for example, in a range of 10 nm to 1000 µm. Other suitable lengths include, for example, from 20 nm to 800 nm, 40 nm to 600 nm, 60 nm to 400 nm, 80 nm to 200 nm, 90 nm to 150 nm, 100 nm to 1 µm, 500 nm to 5 µm, 700 nm to 50 µm, 20 nm to 100 µm , 50 nm to 500 µm, 70 nm to 800 µm, 5 µm to 900 µm, 10 µm to 800 µm, 20 µm to 700 µm, 30 µm to 600 µm, 40 µm to 500 µm, 50 µm to 400 µm, 60 µm to 300 µm, 70 µm to 200 µm, and 80 µm to 100 µm. The length can be, for example, about 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400 nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 950 nm, 1 µm, 10 µm, 20 µm, 30 µm, 40 µm, 50 µm, 60 µm, 70 µm, 80 µm, 90 µm, 100 µm, 150 µm, 200 µm, 250 µm, 300 µm, 350 µm, 400 µm, 450 µm, 500 µm, 550 µm, 600 µm, 650 µm, 700 µm, 750 µm, 800 µm, 850 µm, 900 µm, 950 µm, or 1000 µm.

[0044] The pattern elements can be separated by a gap have a width, for example, in a range of 10 nm to hundreds of micrometer. Suitable gap widths include, for example, from 50 nm to 5 µm, from 100 nm to 1 µm, 200 nm to 800 nm, 300 nm to 600 nm, 400 nm to 500 nm, 100 nm to 100 µm, 150 nm to 200 µm, 200 nm to 500 µm, 300 nm to 700 µm, and 400 nm to 900 µm. The gap width can be, for example, about 10 nm, 20 nm, 30 nm, 40 nm, 50 nm, 60 nm, 70 nm, 80 nm, 90 nm, 100 nm, 150 nm, 200 nm, 250 nm, 300 nm, 350 nm, 400

nm, 450 nm, 500 nm, 550 nm, 600 nm, 650 nm, 700 nm, 750 nm, 800 nm, 850 nm, 900 nm, 950 nm, 1 μm, 2 μm, 3 μm, 4 μm, 5 μm, 6 μm, 7 μm, 8 μm, 9 μm, 10 μm, 50μm, 100 μm, 150 μm, 200 μm, 250 μm, 300 μm, 350 μm, 400 μm, 450 μm, 500 μm, 550 μm, 600 μm, 650 μm, 700 μm, 750 μm, 800 μm, 850 μm, 900 μm, or 950 μm.

[0045] The sacrificial pattern material can be coated on a microtip 18 or an array of microtips and patterned directly onto a surface, for example, the mask layer 12. Suitable microtips include, for example, atomic force microscopy tip, a scanning microscopy tips, solid tips, hollow tips, or nanoscopic tips. For example, the resist pattern 16 can be formed using direct-write patterning methods, such as dip-pen nanolithography. Referring to Figures 9A and 9B, typically, in tip based synthesis methods, such as DPN, the thickness and area of a deposited feature are a function of the tip dwell time.

[0046] The microtip 18 can be coated, for example, with the sacrificial pattern material using any suitable method including, but not limited to, thermal evaporation, spin coating, or by dipping the microtip 18 into the sacrificial pattern material. The sacrificial pattern material can be included in a solution, for example, in a solvent, for example, to facilitate coating. For example, a PEG acetonitrile solution can be used to load the microtips with the sacrificial pattern material (i.e., PEG). The solvent can be evaporated from the sacrificial pattern material upon patterning. Alternatively, the microtip 18 can include a channel or other reservoir to contain the sacrificial pattern 24 material, and the sacrificial pattern material can be dispensed through the channel or a port from the reservoir onto the substrate 10. For example, the microtip 18 can be an evaporator-type microtip. The sacrificial pattern 24 can also be formed using microcontact printing. For example, the sacrificial pattern 24 can be formed by applying the sacrificial pattern material to a microstamp and stamping the sacrificial pattern 24 onto a surface.

[0047] Deposition of the sacrificial pattern 24 using the microtip 18 can be carried out at various humidity levels. For example, higher humidity such as at least about 40%, at least about 60%, at least about 80%, at least about 90%, or at least about 93% can be used. For example, a 93% humidity and a temperature, for example, of about 28^0C can be used for forming the sacrificial pattern 24.

[0048] Electrodes

[0049] Referring to Figures 2A-2D, 4A-4C, and 6A-6D electrodes can be formed using the photomask and conventional photolithography methods. For example, an electrode substrate

can be exposed using a photomask formed by a method in accordance with an embodiment of the invention as a mask and then developed. The electrode pattern can be formed, for example, upon developing of the electrode substrate 10. Electrode leads can be interfaced with the electrodes using any known methods. For example, conventional lithography using a conventional photomask can be used to wire bond the electrode to the electrode leads. Referring to Figure 6A-6D, electrodes can be assembled into an array of electrodes.

[0050] The electrode can be used, for example, to make electrical transport measurements. Referring to Figure 2E and 4D, transport measurements of a sample, such as polypyrrole (PPy) nanotubes, for example, can be made by dispersing the sample on or below the electrode and measuring the current and voltage.

[0051] Referring to Figures 2D and 7B, a top electrode, for example, can be fabricated using the photomasks of the invention. For example, a top electrode can be formed using conventional photolithography and the photomask over a substrate containing a sample. The top electrode can be used to measure the electrical transport properties of the sample. For example, PPy nanowires (as illustrated in Figure 8C and 8D) can be dispersed on a wafer, for example, a silicon wafer, and then the top electrode can be formed on the wafer, over the PPy nanowires. Referring to Figure 2E, current and voltage measurements can then be made using the top electrode to determine, for example, the electrical transport properties of the PPy nanowires.

[0052] Referring to Figures 4C and 7A, a bottom electrode can also be formed using the photomasks of the invention. For example, a bottom electrode can be formed using conventional photolithography and the photomask. A sample, for example, PPy nanotubes (as illustrated in Figures 8A and 8B) can then be dispersed on top of the electrode. Referring to Figure 4D, the bottom electrode can be used to measure the electrical transport properties of the sample.

EXAMPLES

[0053] The following examples are provided for illustration and are not intended to limit the scope of the invention.

[0054] All DPN-patterning experiments were carried out with an NSCRIPTOR® platform (Nanolnk Inc., Skokie, IL) and commercially available AFM cantilevers. Specifically, Si_3N_4, Type E and Type A AFM cantilevers were used (Nanolnk, Inc., Skokie, IL). All DPN-patterning was carried out under about 93% humidity and at a temperature of about 28^0C.

[0055] All photolithography experiments were carried out with a mask aligner (Q-4000, Quintel) and positive-type photoresist (AZ1518, MicroChemicals). AZ1518 photoresist is reported to include cresol novolak resin and 2,1,5-diazonaphthaaloquinone sulfonic acid esters with 2,3,4-trihydroxy benzophenone in a methoxy-propyl acetate (PGMEA) solvent, have a solids content of 29.9%, viscosity of 34.2 cSt at 25 ^{0}C, absorptivity [l/g*cm] at 398nm of 1.30, maximum water content of 0.5% spectral sensitivity of 310-440 nm, filtration [μm absolute] of 0.2, and provides a film thickness of 2.08 μm at spin speed of 3000 rpm.

[0056] Example 1: Fabrication of a Positive Tone Photomask

[0057] Referring to Figures IA, a positive tone photomask was fabricated using ODT as an etching resist on a gold-over-chromium coated quartz substrate. As illustrated in Figure IA, the chromium layer was disposed on the quartz substrate and the gold layer was disposed on the chromium layer. The gold layer had a thickness of about 10 nm and the chromium layer had a thickness of about 100 nm. A resist pattern of 1-octadecanethiol (ODT, Sigma Aldrich) was formed on the gold layer by DPN using an 18-pen one-dimensional cantilever array.

[0058] The one-dimensional pen array was coated with ODT by thermal evaporation at about 70^{0}C for about one hour. The 18-pen one-dimensional cantilever array was formed from a 26 pen cantilever array (Nanolnk, Skokie, IL), with 8 of the pens deliberately removed to create an array with 16 aligned along a line and evenly spaced pens (550 μm), with two pens separated from the central 16-pen array by 150 μm. This array was used to deposit the ODT pattern onto the gold layer in the form of four parallel straight lines having a width of about 5 μm and a length of 560 μm. The lines were separated by a 5 μm gap. Each of the 16 pens in the array formed a 36 μm long line. The lines of each pen were deposited so as to have a 1 μm long overlap with the line of the adjacent pen. The two separated pens were used to form 36 μm long lines on each side of the 560 μm long line. The offset 36 μm long lines were fiduciary marks for subsequent lithographic events. The 18-pen array was used to form four parallel 560 μm long parallel lines and four offset 36 μm long lines in line with the 560 μm long parallel lines.

[0059] The gold layer was then patterned using the ODT pattern as a mask. The gold layer was patterned by etching with an aqueous etching solution containing 20 mM thiourea, 30 mM iron nitrate, 20 mM hydrochloric acid, and 2 mM octanol for about 10 minutes. The Cr layer was then patterned to form the mask pattern using the ODT pattern and the gold pattern as etching masks. The Cr layer was patterned by etching using a commercially- available Cr

etchant (Transen Inc.). The etched gold pattern was then removed to form a positive-type Cr photomask. Longer etching times of about 1 hour with an aqueous etching solution containing 20 mM thiourea, 30 mM iron nitrate, 20 mM hydrochloric acid, and 2 mM octanol were used to remove the Au pattern, leaving the Cr resist pattern.

[0060] Example 2: Fabrication of a Negative Tone Photomask

[0061] Referring to Figure IB, a negative tone photomask was fabricated on a gold-over-chromium coated quartz substrate. As illustrated in Figure IB, the chromium layer was disposed on the quartz substrate and the gold layer was disposed on the chromium layer. The gold layer had a thickness of about 10 nm and the chromium layer had a thickness of about 100 nm. A DPN-generated pattern of poly(ethylene glycol) PEG was formed on the gold layer as a sacrificial pattern. A one-dimensional pen array was used to pattern the PEG on the gold layer. The one-dimensional pen array was coated with PEG (MW 2000, Sigma Aldrich) by tip dipping in 5 mg/ml PEG acetonitrile solution for about 30 seconds. The substrate was then passivated with a 1 mM ODT hexane solution to form an ODT resist pattern of ODT self-assembled monolayers between the PEG pattern. PEG was washed away with dichloromethane. The gold and chromium layers were etched by exposure to the same etching solution. The Au layer was etched using the ODT resist pattern as an etching mask. The Cr layer was etched using the ODT resist pattern and the etched gold layer as etching masks. After etching, a negative type Cr photomask was obtained. (Figure IB).

[0062] Example 3: Fabrication of a Negative Tone Photomask

[0063] Referring to Figure 1C, a negative tone photomask was formed using a lift-off process. Quartz substrates were prepared by initially spin coating with hexamethyldisilazane (HMDS) at 5000 rpm for about 20 seconds. The coated substrates were then baked at 100^0C for about 10 minute. A sacrificial PEG pattern was formed on the HMDS spin-coated quartz glass using DPN. The PEG pattern was formed to have a thickness greater than about 100 nm. DPN-generated PEG patterns were formed using one-dimensional pen arrays. The one-dimensional pen arrays were coated with PEG (MW 2000, Sigma Aldrich) by tip dipping in 5 mg/ml PEG acetonitrile solution for about 30 seconds.

[0064] HMDS is generally used to enhance adhesion of the mask material on quartz glass. The adhesion property between Cr and HMDS can prevent peeling of the Cr layer on the HMDS spin-coated quartz glass by gentle rubbing. In addition, HMDS layer makes a quartz surface hydrophobic, so that PEG is not spread out during and after DPN patterning.

[0065] A 50 nm thick layer of Cr was subsequently deposited on the PEG patterned substrate. The PEG pattern was lifted off the substrate by sonicating in water, which removed the PEG pattern and the portion of the Cr layer disposed on the PEG pattern. As a result, a Cr mask pattern was formed, thereby forming a negative tone Cr photomask.

[0066] Example 4: Photomask Design

[0067] Referring to Figures 3A and 3B, a positive type photomask and a negative type photomask were formed. A PEG pattern was formed on a gold-coated, chromium-coated substrate using DPN. The substrate including the PEG pattern was passivated with ODT. The PEG pattern was removed, leaving the ODT resist pattern disposed on the gold layer. The gold and chromium layers were etched using the ODT resist pattern as an etching mask. The ODT resist pattern and the etched gold layer were then removed, thereby forming the photomask.

[0068] Referring to Figure 3A, the positive type photomask had a PEG pattern consisting of four parallel lines separated by a gap. Each line had a length of about 36 µm and a width of about 5 µm. The corresponding photomask had a mask pattern consisting of four parallel lines separated by a gap. Each line had a length of about 37 ± 0.1 µm and a width of about 5.5 ± 0.1 µm.

[0069] Referring to Figure 3B, the negative type photomask had a PEG pattern consisting of 6 lines. Each line had a width of about 1.5 µm. The straight center lines of the pattern each had a length of about 34 µm. The corresponding photomask had a mask pattern consisting of six lines oriented as in the PEG pattern. Each line had a width of about 2.6 ± 0.1 µm. The straight center lines of the pattern each had a length of about 34. 8 ± 0.1 µm.

[0070] This example illustrates that the mask pattern of the DPN-generated photomask had structures that were qualitatively similar to the intended design.

[0071] Example 5: Bottom Electrode for PPy **Nanotube Electrical Measurement**

[0072] Referring to Figures 2A-2D, four interdigitated electrodes were formed using a positive-type photomask. The electrode was formed using conventional photolithography using the positive-type photomask (shown in Figure 2B) formed by the method illustrated in Figure IA and described in Example 1. Referring to Figure 2C, the 5 µm wide and 0.56 mm long four-line Au electrode was made on a silicon substrate 10 using the DPN generated photomask shown in Figure 2B and conventional photolithography.

[0073] Referring to Figure 2C and 2D, the resulting electrode had four 560 μm long, 5 μm wide parallel straight lines. Adjacent lines were separated by 5 μm gap. Referring to Figure 2D, in order to connect the electrode fabricated by DPN generated photomask to a current-voltage measurement instrument, the electrode was wire-bonded to the current-voltage instrument using conventional photolithography and a conventional photomask. As described above in Example 1, the photomask included fiduciary markings formed by two offset pens of the one-dimensional pen arrays. The fiduciary marks can be used as alignment markings for bonding the electrode to the current-voltage meter.

[0074] Referring to Figure 2E, the electrical properties of PPy nanotubes (shown in Figures 8A and 8B) were measured using the electrode. PPy nanotubes with 300 nm diameter were dispersed on the electrode as shown in inset image of Figure 2E. I-V curves were measured with and without UV irradiation. The voltage was scanned from -1 to IV with 0.05 V steps. Forward and reverse scans are shown with little apparent hysteresis. The power of the UV lamp was 150 W. The increased current with UV irradiation reflects the characteristic electrical response of PPy nanotubes. A current-voltage meter (2400, Keithley), UV irradiation system (Xe lamp, Ushio, Inc.; lamp power supply LPS-220B, PTI), and custom data-acquisition software were used for the I-V measurements.

[0075] **Example 6: Top Electrode for PPy Nanotube Electrical Measurement**

[0076] Referring to Figures 4B, 4C, and 7B, a top electrode was fabricated using negative tone DPN-generated chromium photomask. Referring to Figure 4B, the photomask included six 1.5 μm wide and 34 μm long electrodes with four alignment marks. The photomask was fabricated using the method illustrated in Figure IB and described in Example 2. A PEG sacrificial pattern 24 was formed on a gold-over-chromium coated substrate by DPN using a single microtip. The substrate including the PEG pattern was then passivated with ODT. Self-assembled monolayers of ODT formed between adjacent elements of the PEG pattern to from an ODT resist pattern on the gold layer. The sacrificial PEG pattern was then removed, leaving the ODT resist pattern. The gold and chromium layers were etched using a wet chemical etching to form a gold pattern and a chromium mask pattern. The ODT pattern and the gold pattern were then removed to form the negative tone photomask (as shown in Figure 4B).

[0077] PPy nanowires (shown in Figure 8C and D) were dispersed on a silicon substrate. The PPy nanowires had diameters of about 30 nm. Referring to Figure 4C, photolithography

and lift-off processes using the DPN generated photomask were used to pattern an electrode onto the silicon wafer including the PPy nanowires. The electrodes were interfaced, using electrode leads, with macroscopically addressable circuitry to perform electrical transport measurements. The electrode leads were formed using conventional photolithography with conventional photomasks. Referring to Figure 4D, the I-V curves of the PPy nanowire were measured with and without UV irradiation, using the same procedure as described in Example 5. Forward and reverse scans showed little apparent hysteresis.

[0078] Example 7: Negative Type **Photomask**

[0079] Referring to Figures 5A to 5D, a negative type photomask was formed using the lift-off process illustrated in Figure 1C. Referring to Figure 5A, a 3 x 3 PEG dot array having dots with diameters of about 2 μm and thicknesses of about 240 nm was formed using DPN on an HMDS spin-coated quartz substrate. The quartz substrate 10 was spin coated with hexamethyldisilazane (HMDS) at 5000 rpm for about 20 seconds. The coated substrate was then baked at 100^0C for about 10 minute. The hydrophobic surface of the HMDS coating can allow for the formation of thicker PEG dots by minimizing the ability of the water meniscus of the microtip to spread. Referring to Figures 9A and 9B, typically, with DPN based synthesis, the area and thickness of a pattern element, such as a dot, will be a function of the microtip dwell time. Accordingly, it can be possible to control the PEG pattern element size using the microtip dwell time.

[0080] Referring to Figure 5B, a chromium layer having a thickness of about 50 nm Cr was then deposited over the substrate including the PEG dot array. Referring to Figure 5C, the PEG dot array was then removed by a lift-off process using sonication in water. The lift-off process removed the PEG dot array and any portion of the chromium layer disposed on the PEG dot array, thereby forming the chromium mask pattern and the negative tone photomask.

[0081] Referring to Figure 5D, the photomask was then used with conventional photolithography to generate a replica array of about 40 nm thick gold dots with a 5 nm thick adhesion layer. The diameter of the bottom of the original PEG mask feature was about 2.6 ± 0.1 μm, matching the diameter of the hole structures in the subsequently formed photomask. The replicated gold dots generated after photolithography using the photomask also had a diameter of 2.6 ± 0.1 μm, and, therefore, closely resembled the original mask hole dimension.

[0082] While the present invention has now been described and exemplified with some specificity, those skilled in the art will appreciate the various modifications, including variations, additions, and omissions that may be made in what has been described. Accordingly, it is intended that these modifications also be encompassed by the present invention and that the scope of the present invention be limited solely by the broadest interpretation that lawfully can be accorded the appended claims.

[0083] All patents, publications and references cited herein are hereby fully incorporated by reference. In case of conflict between the present disclosure and incorporated patents, publications and references, the present disclosure should control.

WHAT IS CLAIMED:

1. A method of forming a photomask, the method comprising:

depositing a sacrificial pattern over a substrate using a microtip or a micro stamp;

forming a mask layer over the combination of sacrificial pattern and substrate; and

removing the sacrificial pattern and the portion of the mask layer disposed on the sacrificial pattern, to form a photomask pattern over the substrate.

2. The method of claim 1, wherein the mask layer comprises a Cr layer.

3. The method of any one of claims 1 or 2, comprising depositing the sacrificial pattern using dip-pen nanolithography.

4. The method of any one of the preceding claims, comprising depositing poly(ethylene glycol) or polypropylene glycol as the sacrificial pattern.

5. The method of any one of the preceding claims, wherein the substrate further comprises an adhesion layer disposed over the substrate upon, and wherein the sacrificial pattern is deposited over the adhesion layer.

6. The method of claim 5, wherein the adhesion layer comprises a material selected from the group consisting of hexamethyldisilazane (HMDS), amino propyl trimethoxyl silane (APTMS), polydimethylsiloxane (PDMS), and mercapto propyl trimethoxyl silane (MPTMS).

7. The method of claim any one of the preceding claims, comprising removing the sacrificial pattern by sonication.

8. The method of any one of the preceding claims, wherein the sacrificial pattern has a thickness greater than a thickness of the mask layer.

9. The method of any one of the preceding claims, comprising depositing the sacrificial pattern using an array of microtips.

10. A method of forming a photomask, comprising:

depositing a resist pattern over a mask layer using a microtip or

microstamp, the mask layer disposed over a photomask substrate; and

patterning the mask layer using the resist pattern as a mask, to form a photomask.

11. The method of claim 10, wherein the mask layer comprises a Cr layer.

12. The method of any one of claims 10 or 11, wherein the resist pattern is formed from a material selected from the group consisting of 1-octadecanethiol, 16-mercaptohexadecanoic acid (MHA), 1-hexadecanethiol (HDT), 11-mercaptoundecanoic acid (MUA), ferrocenyl undecanethiol ,and 1-dodecanethiol (DDT).

13. The method of any one of claims 10 to 12,
wherein the substrate further comprises a supplemental resist layer disposed over the mask layer;
wherein the resist pattern is deposited over the supplemental resist layer;
further comprising patterning the supplemental resist layer using the resist pattern as a mask, to form a supplemental resist pattern; and
wherein the patterning of the mask layer further comprises using the supplemental resist pattern as a mask.

14. The method of claim 13, wherein the supplemental resist layer comprises a layer selected from the group consisting of a gold layer, a silver layer, an aluminum layer, a titanium layer, and a palladium layer.

15. The method of any one claims 10 to 14, comprising depositing the resist pattern using dip-pen nanolithography.

16. The method of any one of claims 10 to 15, comprising patterning the mask layer by etching.

17. A method of forming a photomask, comprising:

depositing a sacrificial pattern over a mask layer using a microtip or microstamp, the mask layer being disposed over a substrate;

depositing a resist material over the combination of sacrificial pattern and mask layer, wherein the resist material selectively forms over the mask layer between

adjacent elements of the sacrificial pattern, thereby forming a resist pattern;

removing the sacrificial pattern; and

patterning the mask layer using the resist pattern as a mask, to form a photomask pattern over the substrate.

18. The method of claim 17, wherein the mask layer comprises a Cr layer.

19. The method of any one of claims 17 or 18, wherein the resist material comprises a material selected from the group consisting of 1-octadecanethiol, 16-mercaptohexadecanoic acid (MHA), 1-hexadecanethiol (HDT), 11-mercaptoundecanoic acid (MUA), ferrocenyl undecanethiol, and 1-dodecanethiol (DDT).

20. The method of any one of claims 17 to 19,
wherein the substrate further comprises a supplemental resist layer disposed over the mask layer;

further comprising patterning the supplemental resist layer using the resist pattern as a mask, to form a supplemental resist pattern; and
wherein the patterning of the mask layer further comprises using the supplemental resist pattern as a mask.

21. The method of claim 20, wherein the supplemental resist layer comprises a layer selected from the group consisting of a gold layer, a silver layer, an aluminum layer, a titanium layer, and a palladium layer.

22. The method of any one of claims 17 to 21, comprising depositing the resist pattern using dip-pen nanolithography.

23. The method of any one of claims 17 to 22, comprising depositing poly(ethylene glycol) or polypropylene glycol as the sacrificial pattern.

24. The method of any one of claims 17 to 23, comprising patterning the mask layer by etching.

25. A photomask formed by the method of any one of the preceding claims.

26. An electrode formed using the photomask of claim 25.

27. A method of forming an electrode, comprising:

depositing a sacrificial pattern over a photomask substrate using a microtip;

forming a mask layer over the sacrificial pattern;

removing the sacrificial pattern and the portion of the mask layer disposed on the sacrificial pattern to form a photomask; and

patterning an electrode substrate using the photomask as an etching mask, to form an electrode.

28. An electrode formed by the method of claim 27.

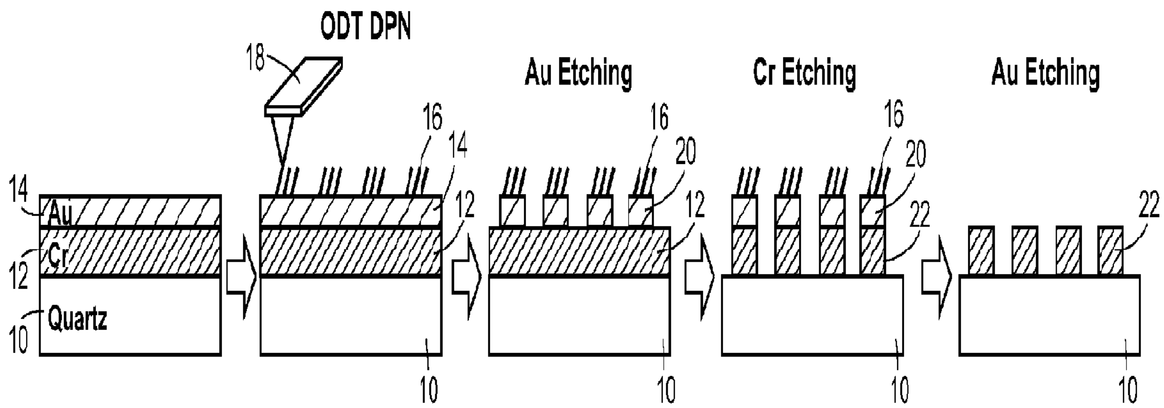


FIG. 1A

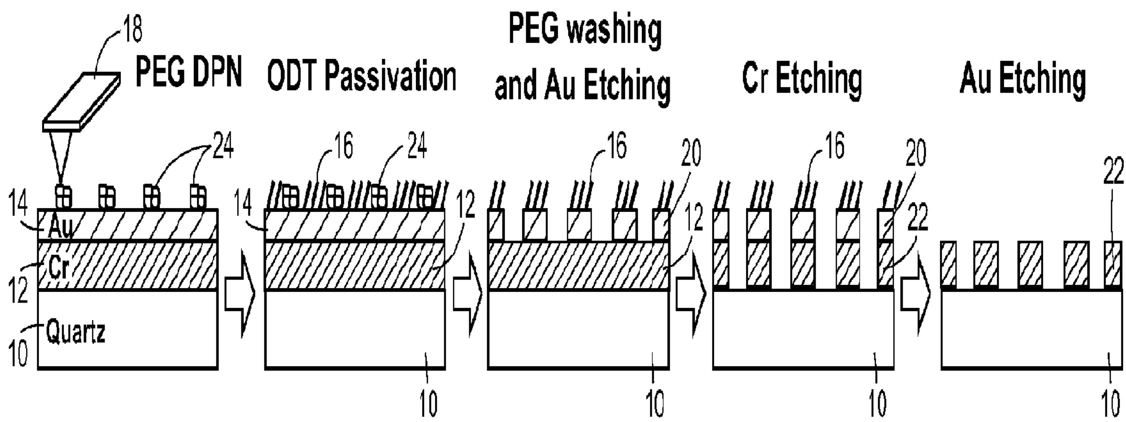


FIG. 1B

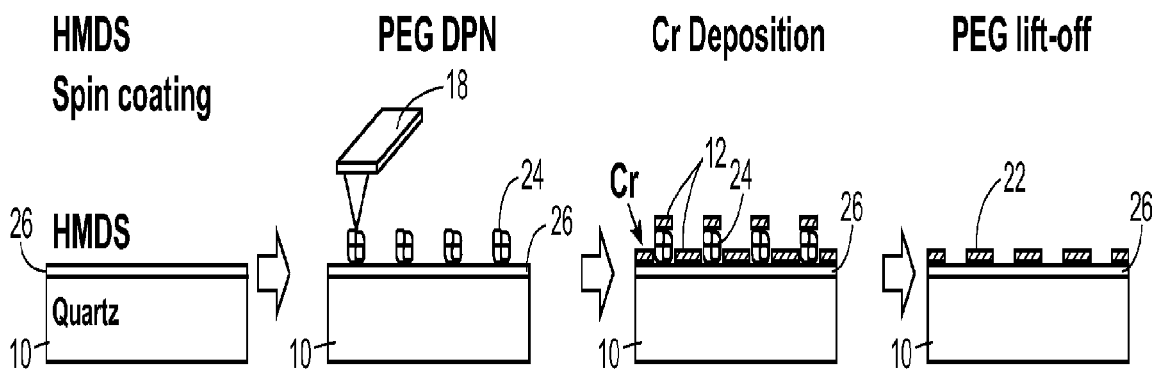


FIG. 1C

FIG. 2A

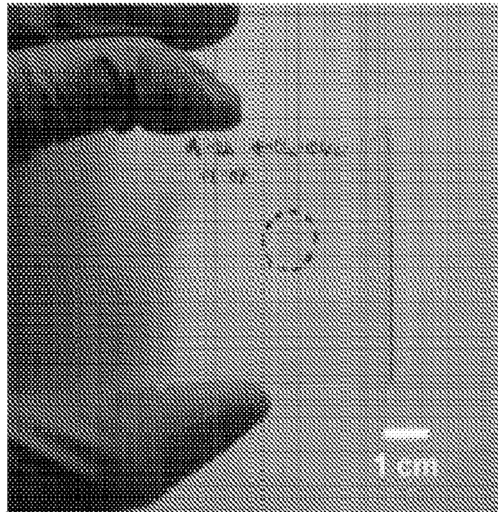


FIG. 2B

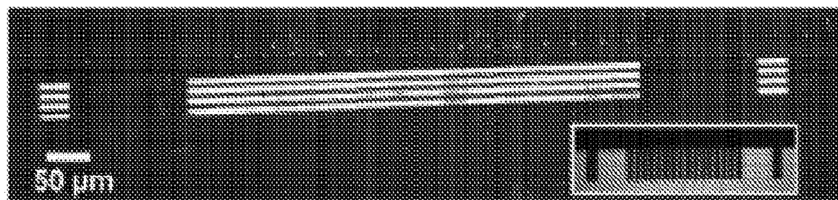


FIG. 2C

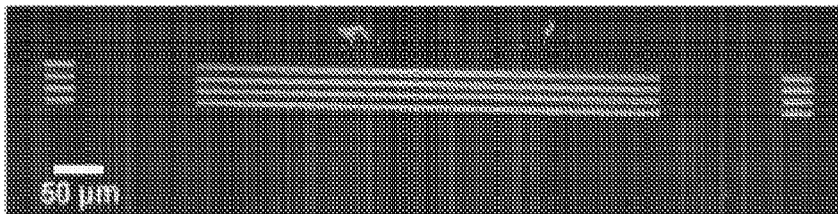
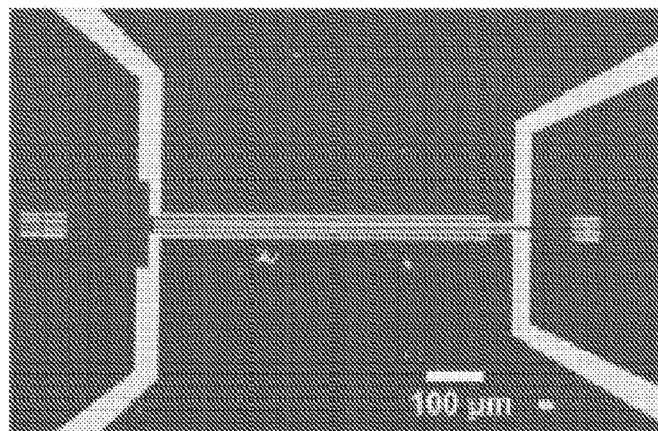


FIG. 2D



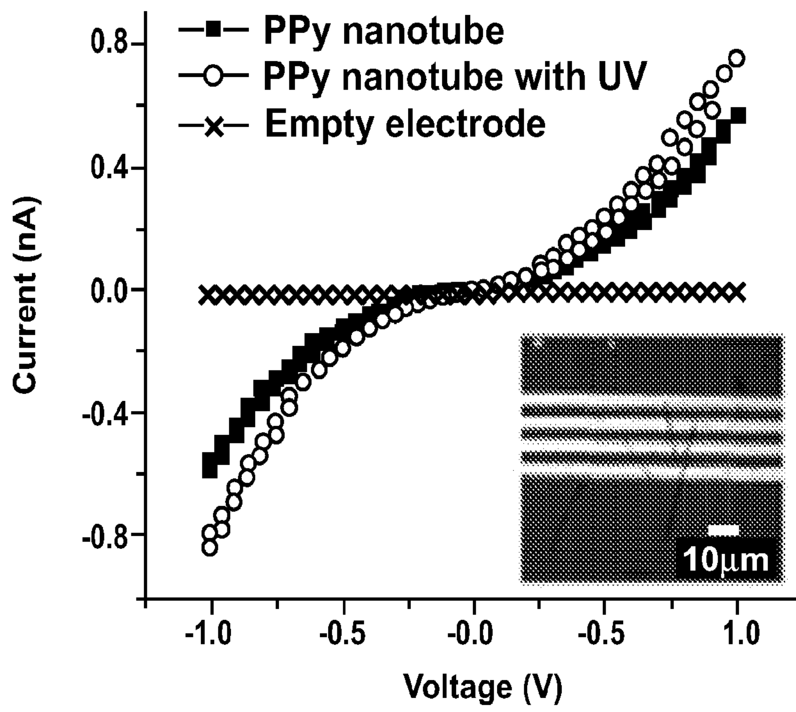


FIG. 2E

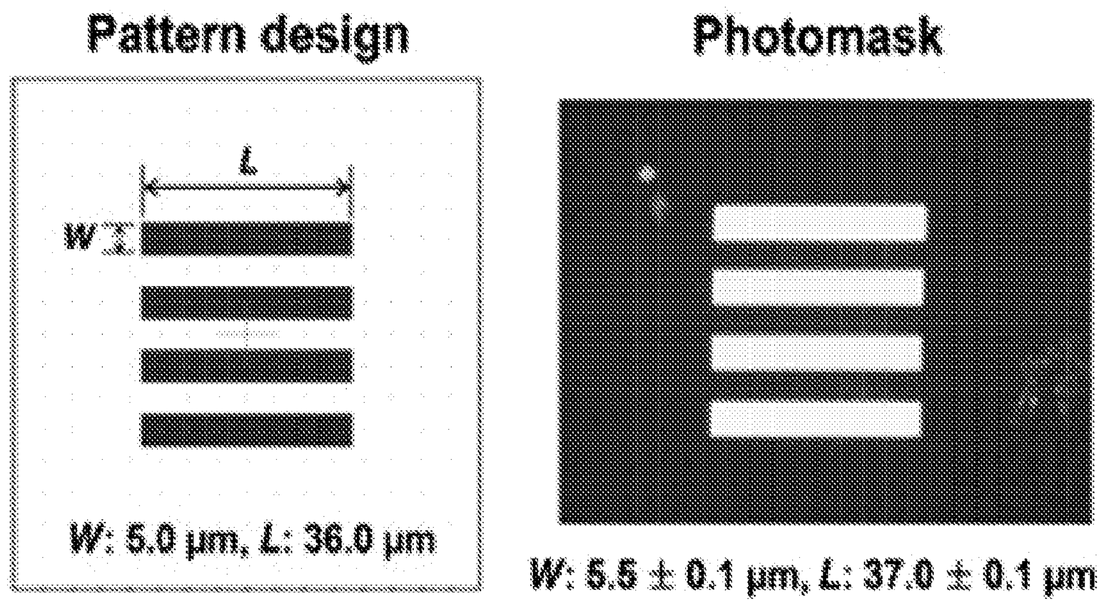


FIG. 3A

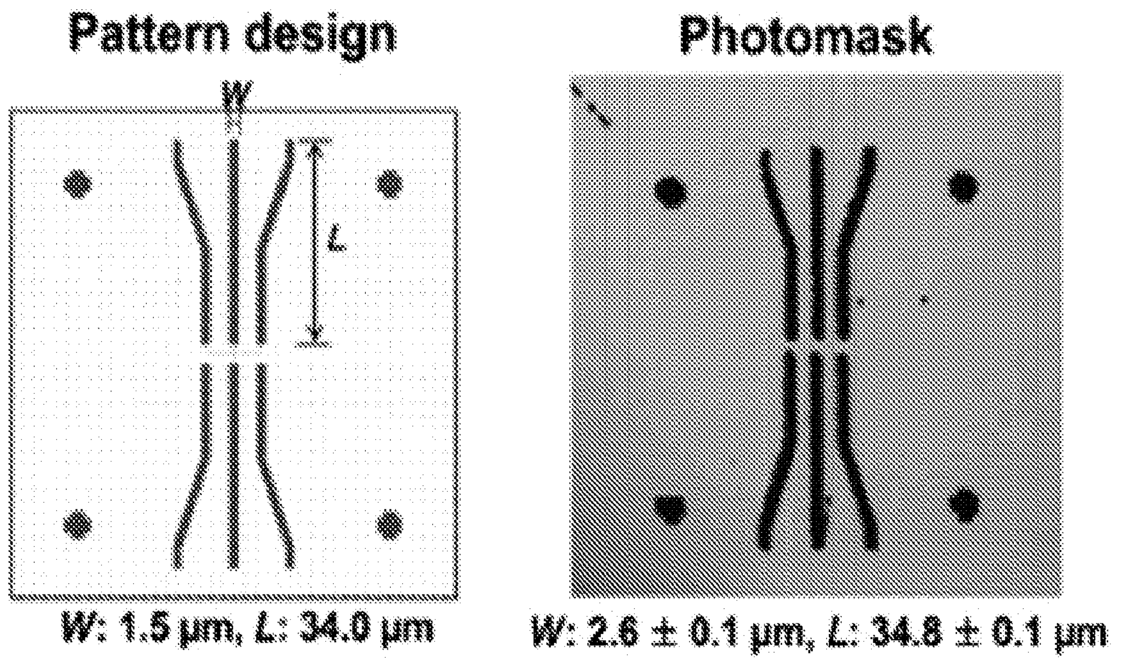


FIG. 3B

FIG. 4A

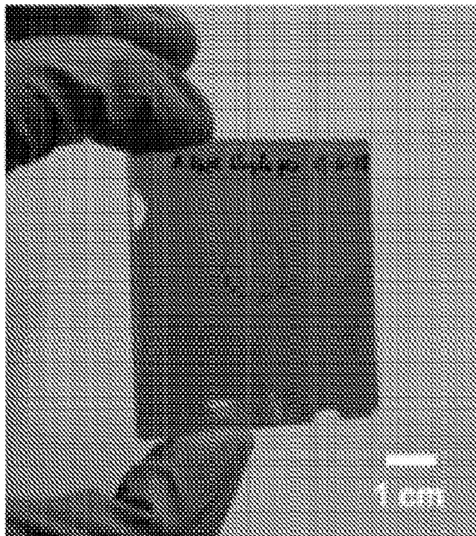


FIG. 4B

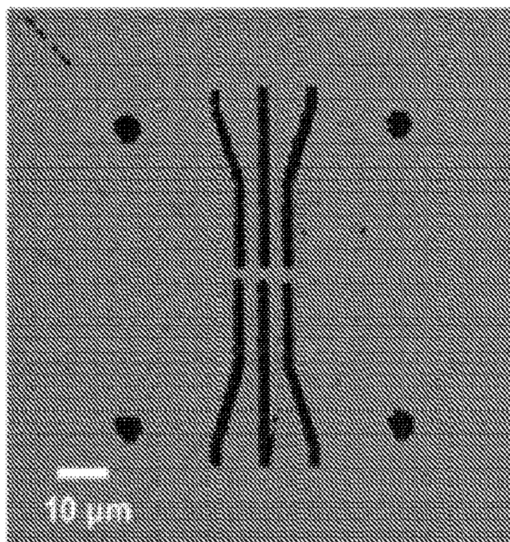
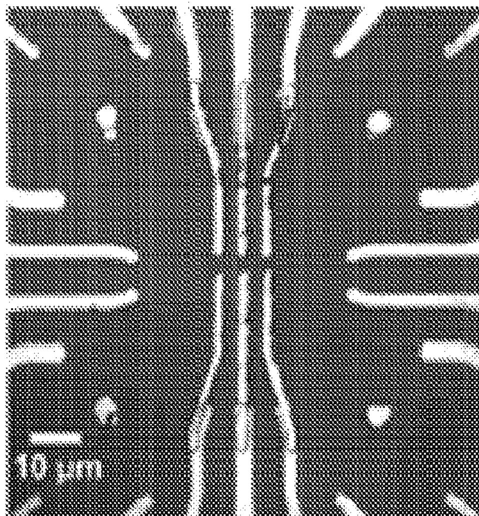


FIG. 4C



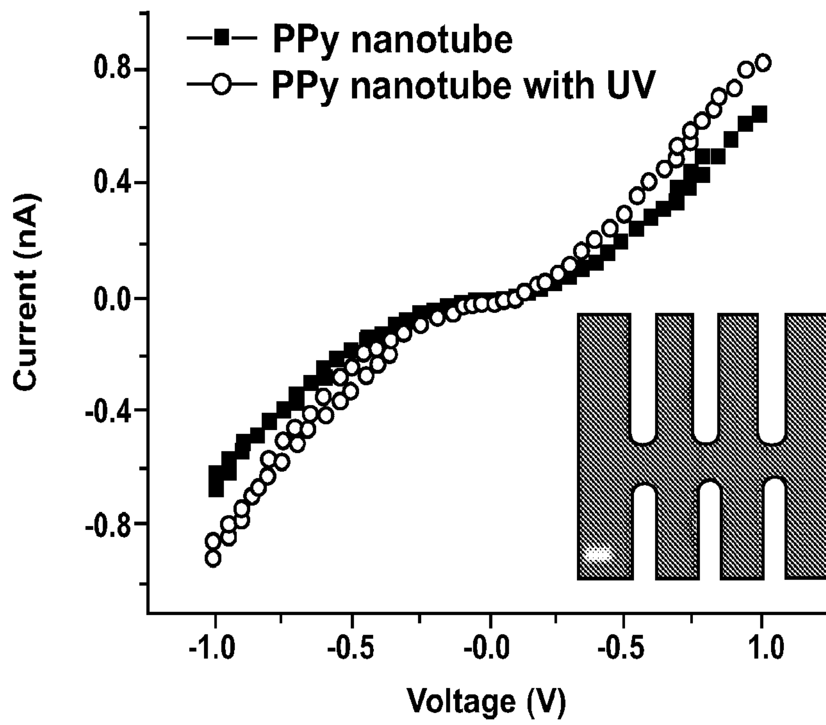


FIG. 4D

FIG. 5A

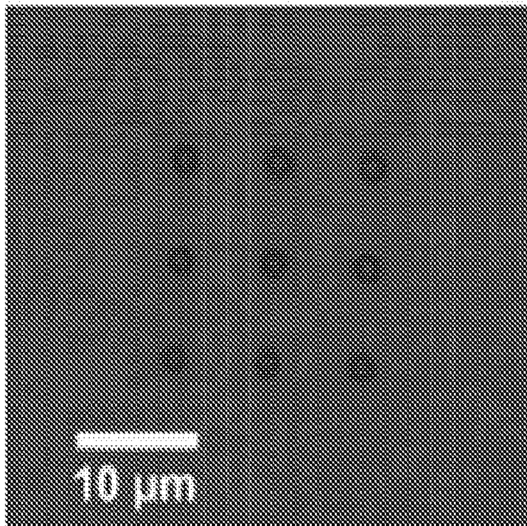


FIG. 5B

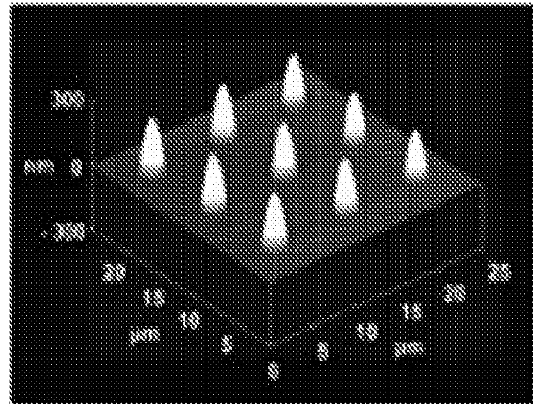


FIG. 5C

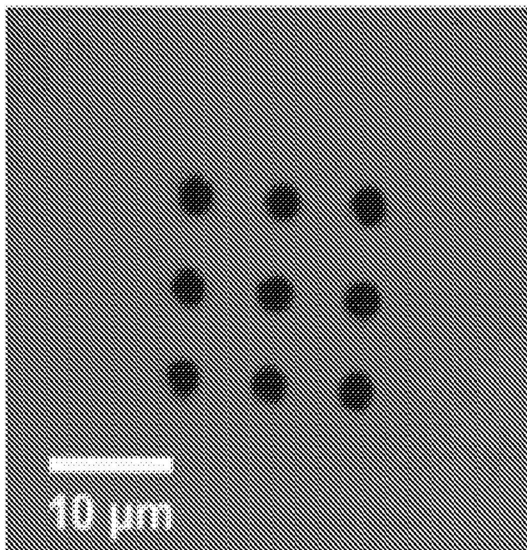
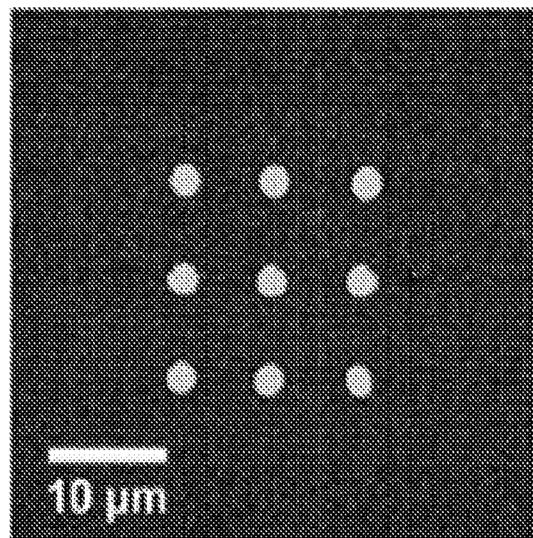


FIG. 5D



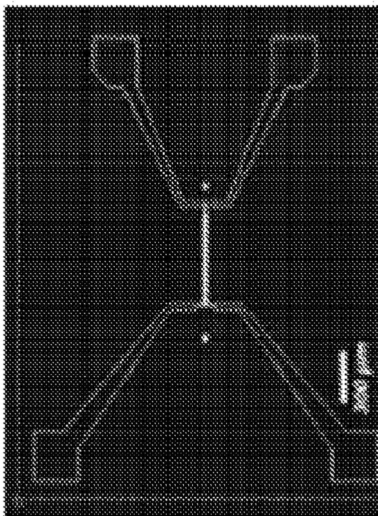


FIG. 6A

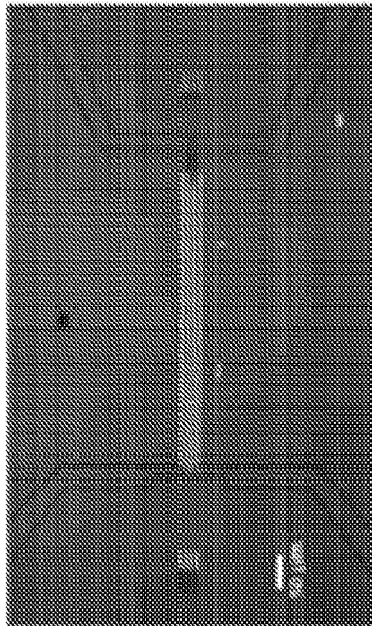


FIG. 6B

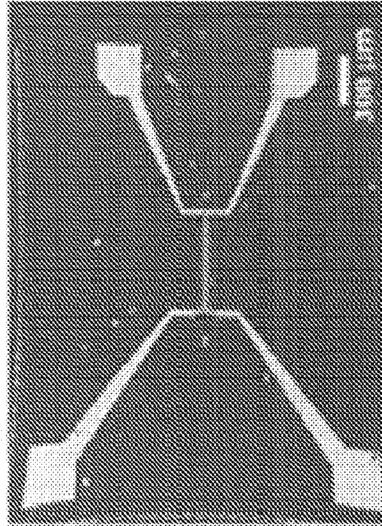


FIG. 6C

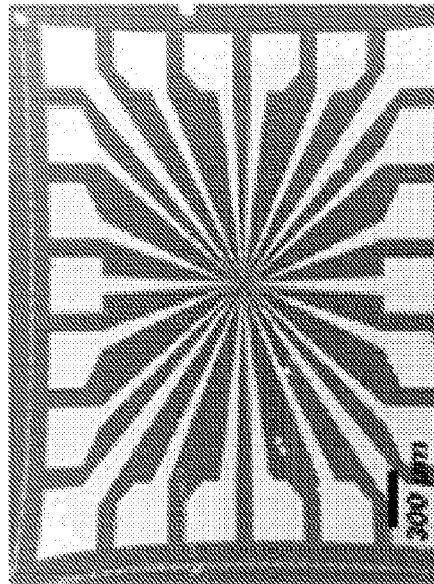
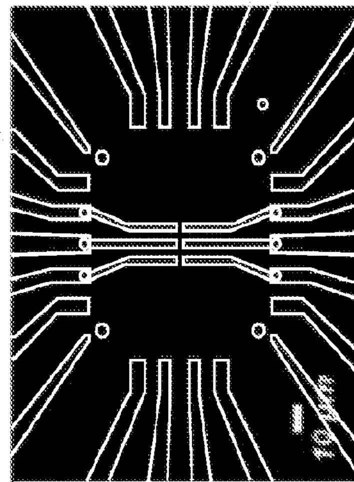


FIG. 6E



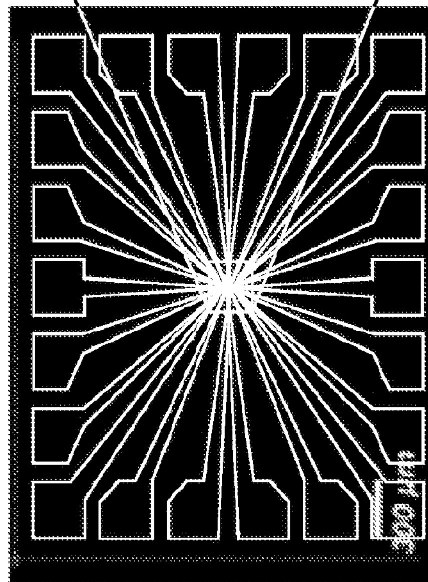


FIG. 6D

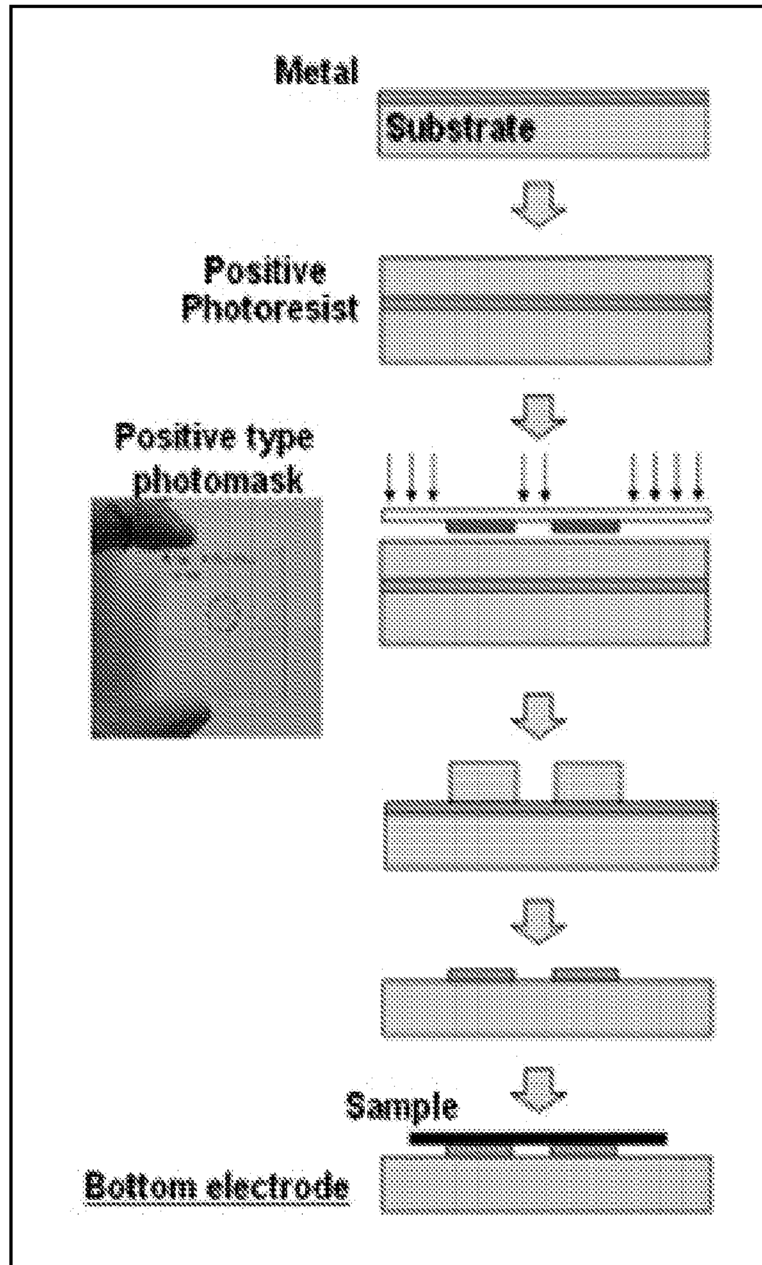


FIG. 7A

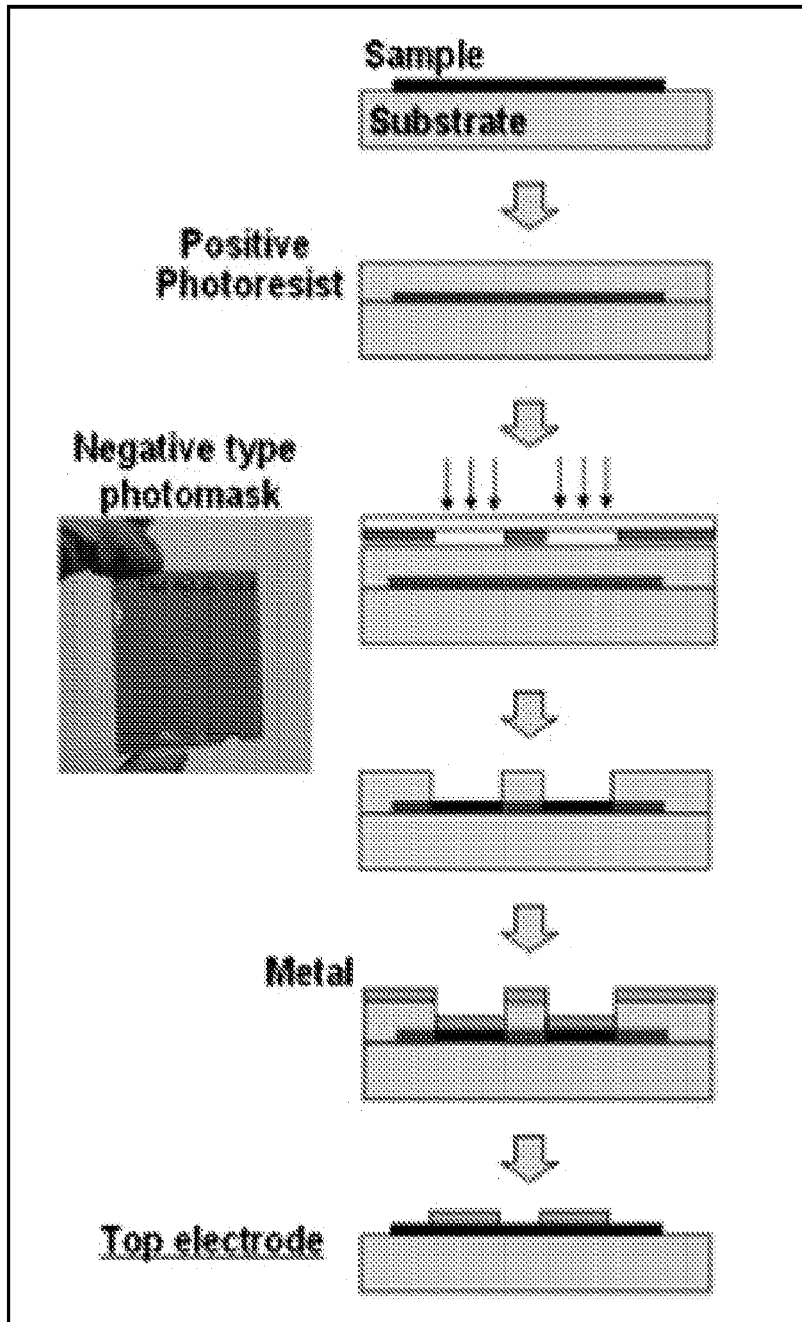


FIG. 7B

FIG. 8A

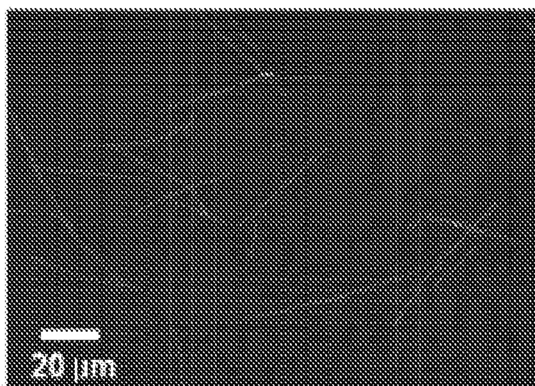


FIG. 8B

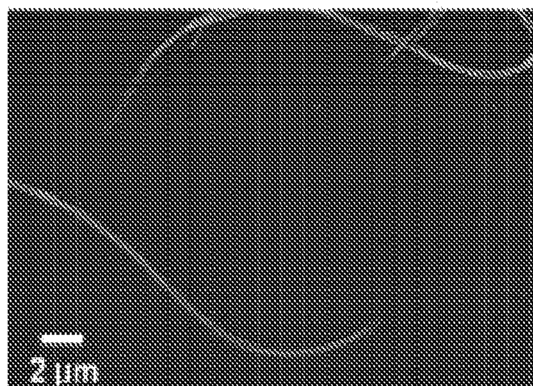


FIG. 8C

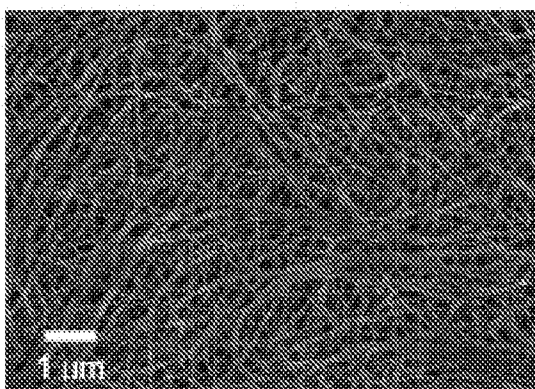
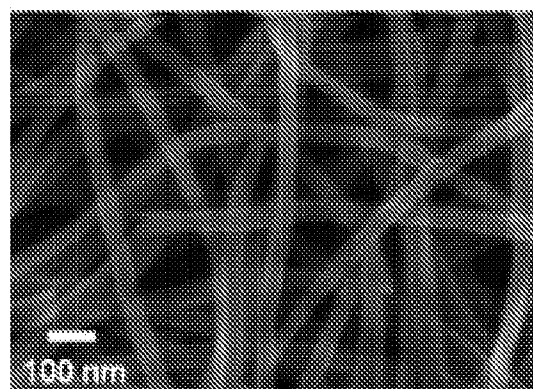


FIG. 8D



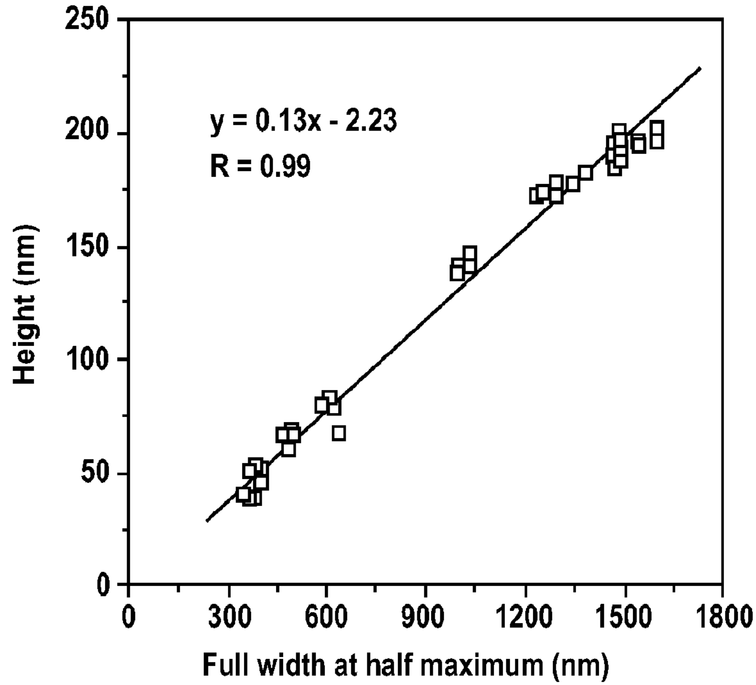


FIG. 9A

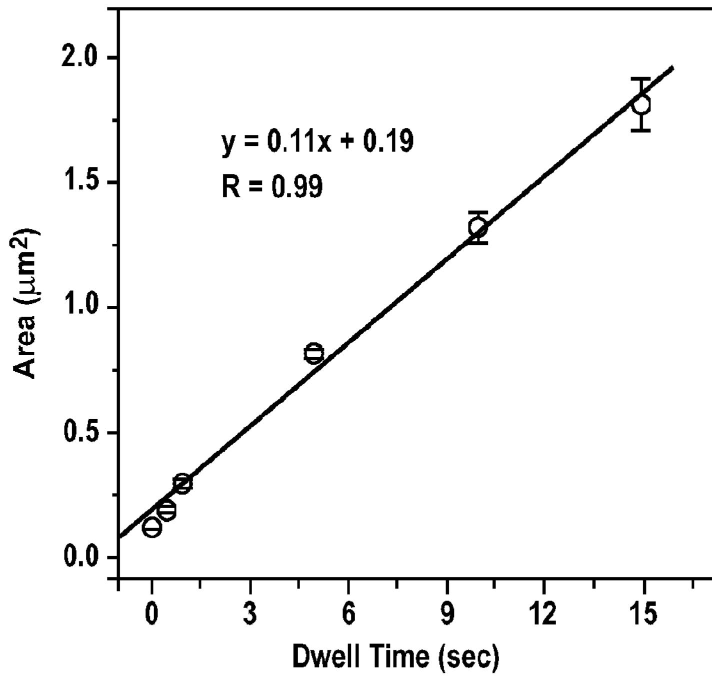


FIG. 9B

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/044903

A. CLASSIFICATIONpF SUBJECT **MATTER**
INV . G03F7/00

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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 practical, search terms used)

EPO-Internal , WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document with indication where appropriate of the relevant passages	Relevant to claim No
X	US 6 518 168 B1 (CLEM PAUL G [US] ET AL) 11 February 2003 (2003-02-11) column 6, lines 14-40 column 6, lines 62-67	1,2,4-7, 25-28
Y	figure 1 column 7, lines 1-5 figure 2 column 7, line 17 column 13, lines 18-24	3,9

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[X] Further documents are listed in the continuation of Box C

[X] 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

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'L' document which may throw doubts on pnoπty 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 pπor to the international filing date but later than the priority date claimed

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Date of the actual completion of the international search	Date of mailing of the international search report
14 October 2009	23/10/2009

Name and mailing address of the ISA/	Authorized officer
European Patent Office, P B 5818 Patentlaan 2 NL - 2280 HV RIjSWijk Tel (+31-70) 340-2040 Fax (+31-70) 340-3016	Perennes , Frederic

INTERNATIONAL SEARCH REPORT

International application No
PCT/US2009/044903

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 2005/255237 AI (ZHANG HUA [US] ET AL) 17 November 2005 (2005-11-17) paragraph [0375] paragraph [0343] paragraph [0249]	10-16, 25-28
Y	paragraph [0359]	3
Y	paragraph [0360]	17-24
Y	paragraph [0011] paragraph [0470]	9
Y	SALAITA K S ET AL: "DPN-generated Nanostructures as Positive Resists for Preparing Lithographic Masters or Hole Arrays" NANO LETTERS, ACS, WASHINGTON, DC, US, vol . 6, no. 11, 27 September 2006 (2006-09-27) , pages 2493-2498, XP002500251 ISSN: 1530-6984 [retrieved on 2006-09-27] scheme 1 page 2494, column 1	17-24
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INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No
PCT/US2009/044903

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			US	2008047930	A1	28-02-2008
US 2006014001	A1	19-01-2006	NONE			