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(54) Title: METHOD OF PATTERNING A SUBSTRATE

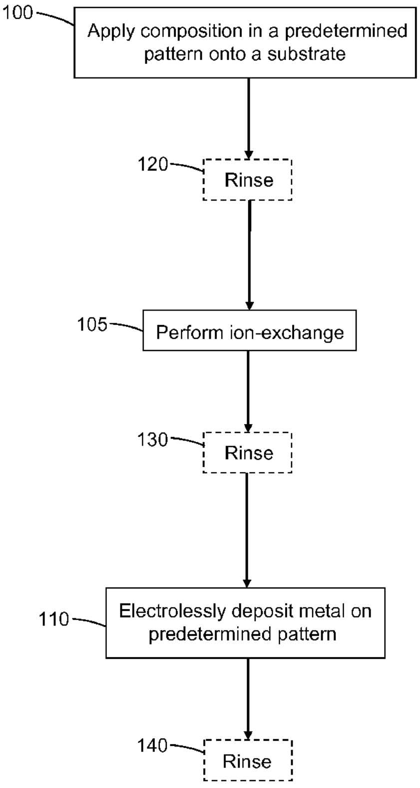

Fig. 5

(57) Abstract: A method of patterning a substrate that includes applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate; and performing ion-exchange between the ionizable substituent and an ionic species.

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METHOD OF PATTERNING A SUBSTRATE

CROSS REFERENCE TO RELATED APPLICATION

This application claims priority to U.S. Provisional Patent Application Serial No. 60/947,527 filed July 2, 2007, the entire contents of which is incorporated by reference herein.

FIELD

This disclosure is related to the preparation of a pattern, and more particularly a metallized pattern, onto a substrate.

BACKGROUND

Formation of small scale features is an ever moving target for the advancement of manufacturing processes. Conductive features of articles are no different and can also require small scale patterning that provides a conductive trace. Electroless deposition is a plating method that is used for the fabrication of micro-scale features. The chemistry and process of electroless deposition has been established for quite some time, and is generally commercially available.

SUMMARY

Disclosed is a method of patterning a substrate that includes the steps of applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate; and performing ion-exchange between the ionizable substituent and an ionic species.

Disclosed is a method of generating a metal pattern onto a substrate that includes the steps of applying a organic composition that includes zinc diacrylates in a predetermined pattern onto a substrate, polymerizing the organic composition with UV radiation, rinsing the polymerized organic composition with deionized water at least 55 degrees C, performing ion-exchange between the polymerized organic composition and a bath containing a silver salt, rinsing the ion-exchanged polymerized organic composition in deionized water, and performing electroless copper plating upon the ion-exchanged polymerized organic composition.

Disclosed is a method of patterning a substrate that includes applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate; rinsing the patterned substrate; performing ion-exchange between the ionizable substituent and an ionic species; rinsing the ion-exchanged substrate; performing electroless deposition on the ion-exchanged substrate; and rinsing the substrate.

Disclosed is a method of patterning a substrate that includes applying a radiation curable organic composition to a substrate; curing at least a portion of the organic composition; removing the uncured portion to form a pattern of a cured organic composition; and performing ion-exchange to replace the ionizable substituent with an ionic species.

An article that includes a substrate; a patterned organic composition; and a patterned metallic coating, wherein the patterned organic composition is covered with the patterned metallic coating forming an overall feature, and wherein the overall feature has a width that is at least about 1 μm wide and at least 20 nm high. Also disclosed are such articles wherein the metallic coating has a thickness of at least about 1 Å.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 illustrates an exemplary method as disclosed herein.

Figure 2 illustrates an exemplary method as disclosed herein.

Figure 3 illustrates an exemplary method as disclosed herein.

Figure 4 illustrates a substrate after a method disclosed herein has been performed thereon.

Figure 5 illustrates an exemplary method as disclosed herein.

Figures 6a, and 6b illustrate portions of the exemplary method described in Example 1.

Figure 7a and 7b illustrate the result of the exemplary method described in Example 2.

Figure 8 illustrates the result of the exemplary method described in Example 3.

Figures 9a, 9b, 9c, and 9d illustrate portions of the exemplary method described in Example 4.

Figures 10a, and 10b illustrate portions of the exemplary method described in Example 5.

DETAILED DESCRIPTION

It is to be understood that embodiments beyond what are mentioned here are contemplated and may be made without departing from the scope or spirit of the present disclosure. The following detailed description, therefore, is not to be taken in a limiting sense.

All scientific and technical terms used herein have meanings commonly used in the art unless otherwise specified. The definitions provided herein are to facilitate understanding of certain terms used frequently herein and are not meant to limit the scope of the present disclosure.

Unless otherwise indicated, all numbers expressing feature sizes, amounts, and physical properties used in the specification and claims are to be understood as being modified in all instances by the term “about.” Accordingly, unless indicated to the contrary, the numerical parameters set forth in the foregoing specification and attached claims are approximations that can vary depending upon the desired properties sought to be obtained by those skilled in the art utilizing the teachings disclosed herein.

The recitation of numerical ranges by endpoints includes all numbers subsumed within that range (e.g. 1 to 5 includes 1, 1.5, 2, 2.75, 3, 3.80, 4, and 5) and any range within that range.

As used in this specification and the appended claims, the singular forms “a”, “an”, and “the” encompass embodiments having plural referents, unless the content clearly dictates otherwise. As used in this specification and the appended claims, the term “or” is generally employed in its sense including “and/or” unless the content clearly dictates otherwise.

Disclosed herein is a method of patterning a substrate. Patterning a substrate generally refers to a coating on a surface which does not have a constant thickness. In one embodiment, patterning a substrate can generally refer to a pattern of thinner and thicker regions. In one embodiment patterning a substrate generally refers to coating only selected regions of a substrate with a material. The selected regions can exhibit a regular or repeating geometric arrangement on the substrate, a random arrangement on the substrate, or an arrangement that is neither random nor repeating but is a specific design which includes or lacks symmetry or repeating shapes. A patterned substrate may have material on only one region of the substrate surface, or it may exist on more than one region of a substrate surface, but a patterned substrate does not have material on all regions of the substrate surface.

The substrate that is utilized in a method as disclosed herein or part of an article that is disclosed herein can be prepared from any suitable material. A substrate for use in a method disclosed herein can be flexible or rigid. In some embodiments, the substrate can be made of metal. Examples of metal materials that can be included in substrates include, but are not limited to, indium, and lead.

The substrate can also be prepared from a polymer material or more than one polymer material. Examples of polymer materials that can be included in substrates include, but are not limited to, thermoplastic polymers. Examples of thermoplastic polymers include, but are not limited to, polyolefins, polyacrylates, polyamides, polycarbonates, polysulfones, polyethersulfones, and polyesters. Further examples of thermoplastic polymers include polyethylene, polypropylene, polystyrene, poly(methylmethacrylate), polycarbonate of bisphenol A, poly(vinyl chloride), poly(ethylene terephthalate) (PET), poly(ethylene naphthalate (PEN), and poly(vinylidene fluoride).

The substrate can also be prepared from a glass material, glass-ceramics, ceramics, semiconductors, or combinations thereof. Examples of useful glasses include, but are not limited to, silicates, germanates, phosphates, and chalcogenides. Glass-ceramics that include a crystallized microstructure can also be useful as substrate materials. Glass-ceramics offer the ease of glass-formability, together with high strength and toughness. Substrates can also include ceramics. Examples of useful ceramics include oxides, nitrides, borides, and carbides. Substrates can also include semiconductors. Examples of useful semiconductors include, but are not limited to, Group IV elements, binary compounds of Group II and Group VI elements, binary compounds of Group III and Group V elements, and their various alloys. Substrates can also be prepared from more than one class of materials, including, but not limited to those discussed above. For example, substrates can include a semiconductor crystal with a coating of a glass or ceramic material.

The particular type of substrate utilized can be chosen based at least in part on a number of factors, including but not limited to, the patterning method that will be utilized, the final application of the article that is being produced, or combinations thereof.

FIG. 1 illustrates an exemplary method of patterning a substrate that includes a step of applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate **100**, and a subsequent step of performing ion-exchange between the ionizable substituent and an ionic species **105**.

The step of applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate, **100**, can be accomplished using any technique known to one of skill in the art for applying a composition onto a substrate in a predetermined pattern. The step of applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate is also referred to herein as applying a composition in a predetermined pattern onto a substrate. One of skill in the art, having read this specification, will be aware of various techniques that can be utilized in this step.

Exemplary techniques for creating a pattern on a substrate include, but are not limited to, die coating, stamping, micro-replication, jet printing (such as ink jet printing), scribing, screen printing, adhering, flexography, embossing, thermal transfer, laser induced thermal imaging (LITI), photolithography, photo-patterning, and molding. In an embodiment, a step of applying a composition in a predetermined pattern onto a substrate includes stamping, ink jet printing, micro-flexographic printing, micro-replication, laser induced thermal imaging, and molding.

In one example, the step of applying a composition in a predetermined pattern onto a substrate does not involve any subtractive process being performed on the substrate. For example, in exemplary embodiments, a step of applying a composition in a predetermined pattern does not include etching or the application of a full layer followed by patterning of the full layer to remove a portion of the layer.

In an example, the step of applying a composition in a predetermined pattern onto a substrate **100** includes more than one step. An example of a multi step process to create a pattern of a composition on a substrate is illustrated in **FIG. 2**. The first step in this exemplary process includes applying a radiation curable organic composition to a substrate without a pattern **101**, curing at least a portion of the organic composition **102,** and then removing the uncured portion to form a pattern of a cured organic composition **103**. Such methods of applying a composition in a predetermined pattern can be advantageously utilized with organic compositions that are curable via the application of ultraviolet (UV) radiation.

In such an embodiment, the step of applying a radiation curable organic composition **101** can be accomplished by any method known to one of skill in the art, including, but not limited to coating methods, such as spin coating, knife coating, bar coating, gravure coating, dip coating, spray coating or die coating. The step of curing at least a portion of the organic composition **102** can be accomplished using a radiation blocking material which will allow only portions of the organic composition to cure. The portions can be allowed to cure by removing the radiation blocking material in those areas or affecting the radiation blocking material so that it does allow the organic composition to cure. In one embodiment, the step of curing at least a portion of the organic composition can be accomplished by utilizing a radiation blocking material that is absent in the areas where the pattern will ultimately exist. The step of removing the uncured portion to form the pattern of cured organic composition **103** can be accomplished by rinsing the substrate in an appropriate solvent. The portions of the organic composition that are cured will be crosslinked, and thereby insoluble in the solvent, whereas the portions of the organic composition that are not cured will not be crosslinked, and will therefore be soluble in the solvent.

Applying a composition in a predetermined pattern onto a substrate using techniques such as those discussed above, and others, can be accomplished as is known to those of skill in the art, having read this specification.

As discussed above, a first step in a method disclosed herein includes applying an organic composition in a predetermined pattern onto a substrate. In one embodiment, organic compositions that are utilized herein are radiation curable organic compositions. Radiation curable organic compositions include those that are cured, or crosslinked via radiation of any kind, including thermal radiation, UV radiation, and electron beam (e-beam) radiation. An exemplary radiation curable organic composition can include an organic composition that is cured with UV radiation. In an example, an organic composition that can be utilized herein need not be radiation curable.

An organic composition that can be utilized herein generally includes at least one polymer precursor that includes an ionizable substituent. Where the organic compositions are radiation curable organic compositions, the composition generally includes at least one polymer precursor that includes an ionizable substituent and at least one photoinitiator. Compositions that can be utilized herein can also include one or more polymer precursors that do not include an ionizable substituent. Some organic compositions that are utilized herein generally include at least one polymer precursor that includes an ionizable substituent; and at least one polymer precursor that does not include an ionizable substituent. Some radiation curable organic compositions that are utilized herein generally include at least one polymer precursor that includes an ionizable substituent; at least one polymer precursor that does not include an ionizable substituent; and at least one photoinitiator.

Organic compositions that can be utilized herein can also include more than one polymer precursor that includes an ionizable substituent. In compositions having more than one polymer precursor that includes an ionizable substituent, the at least two polymer precursors can include a different polymer precursor portion, a different ionizable substituent, or a different polymer precursor portion and a different ionizable substituent. In embodiments where the organic composition is a radiation curable organic composition, the polymer precursors can include any kind of polymer precursors that can be cured by the application of radiation when included in a radiation curable organic composition. Polymer precursors that can be cured by the application of radiation include those that are partially cured by the application of radiation. Organic compositions that need not be radiation curable can include polymer precursors that will not dissolve in the subsequent processing steps which the substrate and the patterned organic composition are subjected to.

Exemplary polymer precursors (those that can include an ionizable substituent, and those that do not include an ionizable substituent) that can be used in radiation curable organic compositions include, but are not limited to UV curable compositions. In an embodiment, the radiation curable organic compositions can include materials such as acrylates, methacrylates, epoxies, olefins and combinations thereof. In one embodiment, acrylate polymer precursors are utilized in a radiation curable organic composition.

Exemplary polymer precursors (those that can include an ionizable substituent, and those that do not include an ionizable substituent) that can be used in organic compositions that are not necessarily radiation curable include, but are not limited to UV curable compositions. In an embodiment, the radiation curable organic compositions can include materials such as acrylates, methacrylates, epoxies, olefins and combinations thereof.

Polymer precursors can include monomers, oligomers, or combinations of both monomers and oligomers. At least one monomer and at least one oligomer can be utilized in an organic composition that can be utilized herein. In one example, monomers can be utilized to enhance the solubility of oligomers, if an oligomer(s) is included in an organic composition. In compositions that include at least one monomer and at least one oligomer, the composition can be solidified to initiate polymerization of the composition.

At least one polymer precursor in an organic composition utilized herein includes at least one ionizable substituent. An ionizable substituent is a portion of the compound that can take part in an ion exchange process. The portion of the polymer precursor that takes part in an ion exchange process generally includes a cation or an anion, or a portion that can be made to be cationic or anionic. Examples of cations include, but are not limited to H^+, Zn^{+2}. Examples of ionizable substituents include, but are not limited to, carboxylic acids, phosphonic acids, and acrylic acids. As utilized herein, carboxylic acid ionizable substituents include –COOH groups, -COOZnOOC- groups, -COOMOOC- groups, where M refers to a metal ion having a positive 2 charge. In a polymer precursor that includes a –COOZnOOC- group, the Zn has a +2 charge, and can take part in an ion exchange process.

Generally, the ionizable substituent does not include or is not a material that can function as a catalyst for electroless deposition. Many materials that can function as catalysts for electroless deposition are relatively expensive. The methods disclosed herein offer an advantage in processing costs because the relatively expensive electroless deposition catalysts are only attached to the substrate where the final material will be deposited via the electroless deposition process. This is economically advantageous when compared with a process that coats the entirety of a surface with a composition that contains the catalyst then removes a large portion of it and wastes the catalyst.

Examples of particular polymer precursors that include an ionizable substituent that can be utilized in organic compositions include, but are not limited to, metallic acrylate oligomers such as zinc diacrylate, which is commercially available from Sartomer Inc. (Exton PA) under the tradename CN2404. The metallic acrylate oligomer CN2400, available from Sartomer (Exton PA) can also be utilized.

Examples of particular polymer precursors that do not include an ionizable substituent that can be utilized in radiation curable organic compositions include, but are not limited to, any monomer or oligomer that will not phase separate. Exemplary polymer precursors that do not include an ionizable substituent include, but are not limited to urethane acrylates, hyperbranched oliogomers, polyester acrylate oligomers. One embodiment includes a combination of a polyester and a urethane. Other specific polymer precursors that can be utilized include, but are not limited to pentaerythritol triacrylate, commercially available from Sartomer, Inc. (Exton PA) as SR444, 1,6 hexanediol diacrylate, commercially available from Sartomer, Inc. (Exton PA) as SR238, and a urethane acrylate oligomer available from Cognis (Cincinnati, OH). These two exemplary precursors are advantageously utilized in compositions where CN2404 and/or CN2400 are utilized to enhance the solubility of the metallic acrylates.

Generally, the polymer precursor or precursors can be chosen based at least in part on the substrate that is being patterned. Polymer precursors that form an organic composition that ultimately has a desired adherence to the particular substrate may be advantageous in providing a final article that has desirable properties. The polymer precursor(s) can also be chosen based at least in part on the final application for which the article is to be used, in such a situation, the polymer precursor can be chosen at least in part based on desired characteristics in the final article.

Organic compositions that can be utilized in methods disclosed herein can be solid or liquid. The form of the organic composition can be dictated at least in part based on the materials that are used to make up the composition, the particular technique that will be used to pattern the composition onto the substrate, other processing steps, additional optional processing steps, or some combination thereof. In an example where the organic composition is a liquid, the liquid organic composition can be solidified in order to make the organic composition adhere to the substrate. In an example, the liquid organic composition can be solidified by evaporating the solvent.

The amount of polymer precursor with an ionizable substituent can depend at least in part on the molecular weight of the compounds utilized, and the functionality of the compounds utilized. Organic compositions that can be utilized herein can have 100 percent by weight of a polymer precursor with an ionizable substituent. Organic compositions that can be utilized herein generally have not greater than 30 percent by weight of a polymer precursor with an ionizable substituent. Organic compositions that can be utilized herein can also generally have not greater than 20 percent by weight of a polymer precursor with an ionizable substituent.

Organic compositions that also contain polymer precursors that do not have an ionizable substituent can generally have more (by weight) polymer precursor with no ionizable substituent than polymer precursor with an ionizable substituent. An organic composition that contains polymer precursor with an ionizable substituent and polymer precursor without an ionizable substituent can generally have at least twice as much (by weight) of the polymer precursor without an ionizable substituent as the polymer precursor with the ionizable substituent. An organic composition that contains polymer precursor with an ionizable substituent and polymer precursor without an ionizable substituent can generally have about four times as much (by weight) of the polymer precursor without an ionizable substituent as the polymer precursor with the ionizable substituent.

An organic composition that is a radiation curable organic composition also includes at least one photoinitiator. A photoinitiator is a compound that, under absorption of light, undergoes a photoreaction, producing reactive species. These species are capable of initiating the polymerization of the polymerizable constituents within a radiation curable organic composition. Photoinitiators that are generally used by those of skill in the art can be used in radiation curable organic compositions utilized in methods disclosed herein. Examples of photoinitiators that can be used herein include, but are not limited to, those available commercially from Ciba Geigy under the trade designations DARACUR 1173, DAROCUR 4265, IRGACURE 651, IRGACURE 1800, IRGACURE 369, IRGACURE 1700, and IRGACURE 907, IRGACURE 819; phosphine oxide derivatives include LUCIRIN TPO, which is 2,4,6-trimethylbenzoy diphenyl phosphine oxide, available from BASF (Charlotte, NC); and members of the commercially available Esacure line of products, such as Esacure One 75, available from Sartomer (Exton PA). More than one photoinitiator can also be utilized in a radiation curable organic composition.

A radiation curable organic composition generally contains at least one photoinitiator at a concentration of about 0.1 to 10 weight percent. A radiation curable organic composition can also generally contain at least one photoinitiator at a concentration of about 0.1 to 5 weight percent.

Organic compositions described herein can also contain one or more other useful components that, as will be appreciated by those of skill in the art, can be useful in such compositions. Examples of such additives include, but are not limited to surfactants, pigments, fillers, polymerization inhibitors, antioxidants, and anti-static agents. Such components, if included can be included in amounts known to be effective.

Organic compositions described herein can also contain one or more solvents. The particular solvents and the quantities thereof can be dependent at least in part on the particular type of application technique, the substrate which the composition is being applied to, and combinations thereof. The amount of solvent, and desired characteristics of the organic compositions would be known to one of skill in the art, having read this specification, based on the particular patterning technique that is to be employed.

If an organic composition is to be applied to a substrate using ink jet printing high boiling point solvents may be advantageously utilized. For example, DGMEA (diethylene glycol monoethyl ether acetate), a high boiling point solvent may be utilized in an organic composition. If an organic composition is to be applied to a substrate using a stamping technique, methyl ethyl ketone (MEK), isopropanol, or combinations thereof may advantageously be utilized. It may also be advantageous to utilize a mixture of one or more solvents. For example, a mixture of toluene and isopropanol can provide good coating performance based on the drying characteristics of the toluene and an ability to dissipate a static charge because of the isopropanol. Other application techniques may also have particular solvents or types of solvents that may provide advantageous properties when utilized. One of skill in the art would be aware of the techniques, as well as the types of solvents that could provide advantageous results with those techniques.

The amount of solvent or solvents to be utilized in an organic composition (if they are to be utilized at all) can depend at least in part on the type of application technique that is to be utilized, the substrate which the composition is to be applied to, or some combination thereof.

In an example where the viscosity of an organic composition is important, a polymer precursor, such as a diacrylate can advantageously be used to decrease the viscosity of the organic composition. A polymer precursor, such as diacrylate, can also advantageously be utilized in an organic composition in order to control shrinkage of the patterned composition, and/or the final patterned structures after electroless deposition. Similarly, use of surface functionalized silica can be added to the organic composition in order to reduce shrinkage of the patterned composition, and/or the final patterned structures after electroless deposition. Organic compositions that include longer chain acrylates, for example, can also increase the flexibility and mechanical properties of the patterned composition, and/or the final patterned structures after electroless deposition.

An exemplary radiation curable organic composition that can be utilized in a method as described herein can include an oligomer that includes an ionizable substituent, one or more monomers, and a photoinitiator. Another exemplary radiation curable organic composition that can be utilized in a method as described herein can include an oligomer that includes an ionizable substituent, two monomers, and a photoinitiator. In such a composition, the monomer, or monomers can be chosen to enhance the solubility of the oligomer, which can often be difficult to dissolve.

Referring again to **FIG. 1**, after the organic composition is applied to the substrate, the next step in the method is to perform an ion exchange between the ionizable substituent and an ionic species **105**. Generally, the purpose of the ion exchange step is to replace the ionizable substituent with the ionic species, which is a material that is capable of catalyzing electroless deposition. One of skill in the art, having read this specification, is aware of techniques for carrying out ion-exchange processes. Generally, ion-exchange takes place by replacing one ion for another ion. Generally, in methods disclosed herein, the ion-exchange is a cation exchange. More specifically, the ionizable substituent in the polymer precursor is replaced with another ion, which is capable of catalyzing electroless deposition.

The ion-exchange step can take place via immersing the patterned substrate in a solution containing an ionic species under conditions which will cause the ionic species to replace the ionizable substituent. In one example, the solution that contains the ionic species can be warm. In one example, the solution that contains the ionic species can be at least about 50° C. In one example, the solution that contains the ionic species is generally from about 50° C to about 55° C.

Generally, the conditions include, but are not limited to, the concentration of the ionic species in the solution, the temperature of the solution, other components or lack thereof in the solution, and the solvent in the solution. These, as well as other conditions can also be chosen in order to affect the speed of the process, the efficacy of the process, and other parameters. One of skill in the art, having read this specification, would know how to determine the appropriate parameters necessary to carry out the ion-exchange step.

Generally, the ionic species is one that is suitable to catalyze electroless deposition, or can be made to be suitable to catalyze electroless deposition. Examples of suitable ionic species include, but are not limited to palladium (Pd^{+2}), platinum (Pt^{+2}), rhodium (Rh^{+2}), silver (Ag^{+2} or Ag^{+1}), gold (Au^{+1}), copper (Cu^{+2}), nickel (Ni^{+2}), cobalt (Co^{+2}), iron (Fe^{+2}), and tin (Sn^{+2}). In an example , suitable ionic species include, but are not limited to copper, silver, nickel, gold, platinum, and palladium. When silver (Ag^{+1}) is utilized as the ionic species, the ion-exchange solution can be silver(I)nitrate ($AgNO_3$). The ionic species can also be reduced in order to create a patterned coating of the species on the substrate.

FIG. 3 illustrates an exemplary method disclosed herein, this figure illustrates that after the ion exchange process has been performed **105**, the substrate can then be exposed to an electroless deposition process **110** to replace the ionic species with another metal ion, such as copper, nickel, silver, gold, palladium, platinum, or alloys. **FIG. 4** illustrates the substrate **200** after the exemplary method illustrated in **FIG. 3** has been performed thereon. As seen there, the substrate **200** has patterned organic composition **220** on a first surface **205** (as opposed to a second surface **210**) thereon, and the patterned organic composition **220** is covered, via electroless deposition with the deposit metal coating **225**.

The term "electroless deposition" refers to a process for the autocatalytic plating of metals. It typically involves the use of an electroless plating solution that contains a soluble form of the deposit metal together with a reducing agent. The soluble form of the deposit metal is usually an ionic species or a metal complex (i.e., a metal species coordinated to one or more ligands). Generally, electroless deposition does not include the application of electrical current to a work piece that is being coated. The volume by Mallory and Hajdu describes the process in detail (Electroless Plating--Fundamentals and Applications, Ed. G. O. Mallory and J. B. Hajdu, William Andrew Publishing, Norwich (1990)). Once the substrate is ion-exchanged to include the ionic species, it is immersed in an appropriate plating bath. The ionic species, also referred to as the catalyst catalyzes the deposition of the deposit metal from the plating solution. Once started, plating proceeds by the continued reduction of the solution metal source, catalyzed by its own metal surface, hence the term "autocatalytic."

Metallic deposits that can be formed using electroless deposition include copper, nickel, gold, silver, palladium, rhodium, ruthenium, tin, cobalt, zinc, as well as alloys of these metals with each other or with phosphorous or boron, as well as compounds of these metals with each other or with phosphorous or boron. In one example, the metallic deposit metal includes copper, silver, gold, platinum, palladium, or some combination thereof. The deposit metal and the ionic species can be the same or different.

The reduction of the ionic species can also be carried out separate from the catalytic growth of the deposit metal. Such processes may provide an advantage that they can occur at a faster rate, allowing for processing advantages. The ionic species can be reduced by photo-reduction, chemical reduction, heat reduction, or e-beam reduction. In an example where chemical reduction is utilized, suitable reducing agents include, but are not limited to, formaldehyde, hydrazine, aminoboranes, and hypophosphite.

FIG. 5 illustrates another exemplary embodiment of a method disclosed herein. This method includes optional rinse steps. The first rinse step **120** can occur after the organic composition is patterned onto the substrate. It is thought, but not relied upon that the first rinse step **120** can function to remove organic composition that is not cured, not adhered to the substrate, not within the desired pattern, or some combination thereof. The first rinse step **120** may also function to remove non-tightly bound ions that could interfere with later steps in the method. This first rinse step **120** can generally be carried out with a solvent, for example in a solvent bath. In one example, the first rinse step **120** can be carried out with deionized (DI) water. The DI water can be warm, in one example, the DI water is at least about 50° C. In another example, the DI water is at least about 55° C. In another example, the DI water is at least about 57° C. The first rinse step **120** can also be carried out with an organic solvent, such as methyl ethyl ketone (MEK), or isopropyl alcohol (IPA). The first rinse step **120** can generally be carried out for at least about 5 minutes. In one example, the first rinse step **120** can generally be carried out for at least about 7 minutes. Generally, the rinse step **120** can be carried out with or without agitation of the rinse solution or the substrate within the rinse solution.

In some embodiments, the first rinse step **120** may be performed first as a base rinse using aqueous base solution followed by rinsing with deionized (DI) water. In some embodiments, rinse step **120** can be performed as a 30 second rinse using a 3% aqueous solution of ammonia hydroxide followed by a rinse in DI water. In still other embodiments, aqueous sodium hydroxide can be used in the rinse step **120**, typically at a concentration of 0.2 to 10 wt%, followed by rinsing with deionized (DI) water.

As seen in **FIG. 5**, exemplary methods can also include an optional second rinse step **130**, that can occur after the ion-exchange is performed **105**. It is thought, but not relied upon that the second rinse step **130** can function to remove non-ionically bound ionizable substituents from the substrate. This second rinse step **130** can generally be carried out with a solvent, for example in a solvent bath. In one example, the second rinse step **130** can be carried out with deionized (DI) water. The DI water can generally be room temperature, in one example, the DI water is about 25° C. The second rinse step **130** can generally be carried out for at least about 5 minutes. In one example, the second rinse step **130** can generally be carried out for at least about 7 minutes. Generally, the second rinse step **130** can be carried out with or without agitation of the rinse solution or the substrate within the rinse solution.

Also as seen in **FIG. 5**, exemplary methods can also include an optional third rinse step **140**, that can occur after the electroless deposition is performed **110**. It is thought, but not relied upon that the third rinse step **140** can function to remove electroless deposition chemicals that may remain on the substrate. This third rinse step **140** can generally be carried out with a solvent, for example in a solvent bath. In one example, the third rinse step **140** can be carried out with deionized (DI) water. The DI water can generally be room temperature, in one example, the DI water is about 25° C. The third rinse step **140** can generally be carried out for at least about 5 minutes. In one example, the third rinse step **140** can generally be carried out for at least about 7 minutes. Generally, the third rinse step **140** can be carried out with or without agitation of the rinse solution or the substrate within the rinse solution.

Also disclosed is a method of patterning a substrate that includes applying a radiation curable organic composition to a substrate without a pattern, curing at least a portion of the organic composition, removing the uncured portion to form a pattern of a cured organic composition, and then performing ion-exchange to replace the ionizable substituent with an ionic species.

Also disclosed is a method of patterning a substrate that includes the steps of applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate; rinsing the patterned substrate; performing ion-exchange between the ionizable substituent and an ionic species; rinsing the ion-exchanged substrate; performing electroless deposition on the ion-exchanged substrate; and rinsing the substrate.

Also disclosed herein are articles that are formed using the methods described herein. Exemplary articles that can be fabricated using the disclosed methods generally have patterned organic composition features that are covered with patterned metallic features. In an embodiment, the patterned organic composition features covered with the patterned metallic features, i.e. the metallic coating, are referred to the overall features. Generally, the patterned organic composition features and the patterned metallic features, i.e the overall features can be of any size. In an embodiment, the size of the overall features includes both the height of the patterned organic composition feature and the height of the patterned metallic features. Given this, the size of the overall features can be about 1 micrometer (μm) or larger in width, and about 20 nanometers (nm) or larger in height. In such an article, the size of the patterned organic composition features can be about 1 μm or larger in width and about 20 nm or larger in height. Generally, the depth of the patterned metallic features on the patterned organic composition is about 1 angstrom (Å) or greater. One of skill in the art will understand that a thicker layer of patterned metallic material can be obtained by plating the material for a longer period of time

Articles described and formed herein can have grids of metallic material, and such articles can be used for example, for electromagnetic interference (EMI) shielding. Exemplary articles described and formed herein can have traces of metallic material, and such articles can be used for example, for touch screens, for sensor applications, for circuits, to make reflective indicia, or to create fluid flow devices (where the patterned metallic features can be hydrophilic and the non-patterned portions are hydrophobic). Exemplary articles described and formed herein can have repeating dots or islands of metallic material, and such articles can be used for example, to create shielding effects. The articles include patterns of metallic coatings that can be used to conduct an electric current.

Articles that are described and formed herein can advantageously have the substrate, the organic composition, the metallic material, or some combination thereof matched so that thermal expansion properties of the overall article are similar.

Example 1

An organic composition having an ionizable substituent was prepared by mixing 40 parts by weight of pentaerythritol triacrylate, commercially available as SR444 from Sartomer Company, Inc. of Exton, PA; 40 parts by weight of 1,6 hexanediol diacrylate, commercially available as SR238 from Sartomer; and 20 parts by weight of metallic acrylate oligomer, commercially available as CN2404 from Sartomer. To this was added one to two weight percent of ethyl 2,4,6-trimethylbenzoylphenylphosphinate photoinitiator, commercially available as TPO-L from BASF of Florham Park, NJ.

The organic composition was diluted to the level of a 30 percent by weight solids solution of methyl ethyl ketone (MEK), and then spread with a notch bar onto a flat, non-porous surface. The MEK was allowed to evaporate, resulting in an approximately 20 micron thick coating of the organic composition on the flat surface. This coating was then used to ink the raised surfaces of a rubber hand stamp (seen in **FIG. 6a)**.

The inked stamp was pressed against a substrate made from 2 mil (50 μm) thick polyester film, commercially available as Scotchpar P56 from 3M Company of St. Paul, MN. In this way, the ionizable organic composition was applied in a predetermined pattern to the substrate. Then the organic composition was solidified by subjecting it to UV radiation by passing it through a Fusion UV Curing system model MC-6RQN, which was fitted with an H-bulb providing 30 w/inch, and commercially available from Fusion UV Systems Corp., Rockville, Md. This resulted in a polyester film substrate with a transparent, hard acrylate pattern on it.

The patterned substrate was then rinsed in deionized water (18 megohms) at 57°C for 5 minutes to prepare the surface of the pattern for the next step (the oil bath that the container of deionized water was in was at 57° C, or the specified temperature). An ion-exchange was then performed by bathing the patterned substrate in a 5 wt% solution of silver(I) nitrate in deionized water at 57°C for 5 minutes. After the ion-exchange bath, excess exchange solution was removed by rinsing the ion-exchanged patterned substrate briefly in deionized water at room temperature.

Commercial electroless plating solution ingredients were purchased from Toryon Technologies (Itasca IL) as the products labeled μ-copper 85 A, μ-copper 85 B, μ-copper 85 D, and μ-copper 85 G. The bath was mixed by placing 330 g of DI water in a clean glass beaker or jar. Then, while stirring with a magnetic stir bar, the components were added in the following order: 40 mL µ-copper 85 B, 16 mL µ-copper 85 A, 12 mL µ-copper 85 D, and 0.8 mL µ-copper 85 G. This was allowed to stir for 30 minutes then 2 mL of 37 wt% formaldehyde solution (VWR catalogue number JT2106-4) was added and the solution was mixed for another 15 minutes. To use the solution, it was placed in a beaker inside a stirred oil bath that was maintained at about 47° C and the temperature of the solution was allowed to reach a steady state before use.

The rinsed ion-exchanged patterned substrate was then placed in the electroless copper plating bath described above for 15 minutes. At the conclusion of this bath, the pattern on the substrate had accumulated a strongly adherent layer of metallic copper. **FIG. 6b** shows the substrate, half of which was not placed into the electroless copper planting bath (left side of **FIG. 6b**); and half of which was placed into the electroless copper plating bath (right side of **FIG. 6b**). The electrical continuity of the patterned copper was tested with a multimeter and found to be approximately 0.1 Ohms/cm.

Example 2

A composition was prepared as in Example 1 with the exception that the composition was made from 20 G SR-444, 20 g SR-238, 15 g CN-2404, and 2 g TPO-L. A 20% by weight coating solution of that composition was made by adding 80 wt% of a 70:30 (by weight) toluene:isopropyl alcohol solution. A glass microscope slide was dip coated in the coating solution with a withdraw rate of 0.5 feet per minute leaving a dry coating thickness of about 1 µm.

A stamp was made by solvent assisted embossing of Cyrel (DuPont) plates. This involved placing 3M® brightness enhancing film (BEF, version with ~24 micron spacing between ridge points) on a smooth, level surface with the prism structure pointed up. MEK was squirted on the film, filling the grooves and the Cryel plate was laid on top and left for about 12 hours (over night). While still laminated, the construction was passed through a fusion UV curing system to cure the Cyrel. After the Cryel plate was delaminated, the plate was further cured under a black light for about 12 hours to ensure full curing of the plate.

The stamp was affixed to a glass roll with double sided tape and rolled (rocked once) across the coated glass slide to ink. Then the inked stamp was pressed against (rocked once) on the unprimed side of a 3M® Schotchpar® P56 PET 2 mil film while the film was laying flat leaving a patch of printed lines. The printed film was then passed through the Fusion UV curing system to cure the printed lines.

The film was then soaked in DI water at about 60°C for about 5 minutes. Next, the film was soaked in 5wt% silver nitrate (in water) at about 60°C for about 5 minutes. Then, the film was quickly rinsed in room temperature DI water, followed by the film being placed in a copper electroless plating bath (as in Examples 1) for 20 minutes. After a final DI water rinse and air drying the images seen in **FIG. 7a** and **FIG. 7b** were taken under a microscope and are representative of the sample area. There is about 24 μm between the centers of the lines, which indicates that the width of the features is between about 1 and 10 μm. **FIG. 7a** is backlit, and **FIG. 7b** is top lit.

Example 3

A composition containing 5.0 grams DGMEA, 4.0 grams SR-444 (Sartomer, Exton PA), 4.0 grams SR-238 (Sartomer, Exton PA), 1.8 grams CN-2404 (Sartomer, Exton PA), and 0.2 grams Lucerin™ TPO-L (BASF, Charlotte NC) was prepared. The mixture was found to have a viscosity of approximately 15 centipoise and a surface tension near 31 mN/m. The composition was printed on a Dimatix DMP 2831 (Dimatix, Santa Clara CA) inkjet printing unit to create patterns of varying width lines. The substrate was a 5 mil thick poly[ethylene napthalate] (PEN) available from DuPont Teijin as Q65 (DuPont Teijin, Hopewell VA). The printing platen was set to 60° C to evaporate some of the solvent.

The resulting patterned acrylate was cured by passing it through a Fusion UV Curing system model MC-6RQN fitted with an H-Bulb and nitrogen purge. The resulting cured features were found to have a height above the substrate between 200 and 500 nm.

The patterned substrate was then rinsed in deionized water (18 megohms) at 57°C for 5 minutes to prepare the surface for the pattern for the next step. An ion-exchange was then performed by bathing the patterned substrate in a 5 wt% solution of silver(I) nitrate in deionized water at 57°C for 5 minutes. After the ion-exchange bath, excess exchange solution was removed by rinsing the ion-exchanged patterned substrate briefly in deionized water at room temperature.

The rinsed ion-exchanged patterned substrate was then placed in a conventional electroless copper plating bath (as in Example 1) for 15 minutes. At the conclusion of this bath, the pattern on the substrate had accumulated a strongly adherent layer of metallic copper. An image of the substrate with the metallic copper pattern can be seen in **FIG. 8**. The adherence of the copper pattern was tested by placing a piece of 3M® brand Scotch® tape on the pattern and seeing if the copper would be removed from the substrate onto the tape. The tape did not remove any of the copper pattern.

Example 4

A composition containing 4.0 grams SR-444 (Sartomer, Exton PA), 4.0 grams SR-238 (Sartomer, Exton PA), 1.8 grams CN-2404 (Sartomer, Exton PA), and 0.2 grams Lucerin™ TPO-L (BASF, Charlotte NC) (composition had a 20:20:10:1 ratio by weight of the respective components) was prepared. The mixture was found to have a viscosity of approximately 15 centipoise and a surface tension near 31 mN/m. The composition was printed on a Dimatix DMP 2831 (Dimatix, Santa Clara CA) inkjet printing unit to create patterns of varying width lines. The substrate was a 5 mil thick poly[ethylene napthalate] (PEN) available from DuPont Teijin as Q65 (DuPont Teijin, Hopewell VA). The printing platen was at room temperature and the print head was set to 70° C to lower the viscosity of the solution for consistent ink jet printing.

The resulting patterned acrylate was cured by passing it through a Fusion UV Curing system model MC-6RQN fitted with an H-Bulb and nitrogen purge. The resulting cured features were found to have a height above the substrate between 1 and 2 μm.

The patterned substrate was then rinsed in deionized water (18 megohms) at 57°C for 5 minutes to prepare the surface for the pattern for the next step. An ion-exchange was then performed by bathing the patterned substrate in a 5 wt% solution of silver(I) nitrate in deionized water at 57°C for 5 minutes. After the ion-exchange bath, excess exchange solution was removed by rinsing the ion-exchanged patterned substrate briefly in deionized water at room temperature.

The rinsed ion-exchanged patterned substrate was then placed in a conventional electroless copper plating bath (as in Example 1) for 15 minutes. At the conclusion of this bath, the pattern on the substrate had accumulated a strongly adherent layer of metallic copper. An image of the substrate with the metallic copper pattern can be seen in **FIG. 8**.

Example 5

A mold was made from 3M ESPE Express™ Vinyl Polysiloxane Impression Material (which is a two composition epoxy), a hydrophilic, fast set material. The Impression Material was placed on a substrate and a stamp (shown in **FIG. 9**) was placed in the epoxy. After the material had set, the mold was removed from the stamp. **FIG. 9b** shows the mold that was formed using this process.

A solvent free organic composition made having a 20:20:10:1 ratio by weight of SR444 (Sartomer, Exton PA), SR238 (Sartomer, Exton PA), CN2404 (Sartomer, Exton PA), and TPO-L (BASF, Charlotte NC) was applied via pipette to the mold. The filled mold was then laminated between two sheets of 10mil thick polyethylene terephthalate (PET) film. A multilayer article having the following structure was obtained: 10 mil PET/organic composition/mold /10 mil PET.

The laminate construction was then passed through a Fusion UV Curing system model MC-6RQN (Fusion UV Systems, Inc. Gaithersburg MD) which was fitted with an H-Bulb. The composition was cured and the construction was peeled apart. **FIG. 9c** shows the molded material (adhered to one of the 10 mil PET films) after delamination from the mold. Due to the brittleness of the thick cured material some cracking occurred when the construction was pulled apart.

The cured material on the PET film was then subjected to electroless deposition. The substrate was first rinsed in deionized water (18 megohms) at 57°C for 5 minutes to prepare the surface of the pattern for the next step. An ion-exchange was then performed by bathing the patterned substrate in a 5 wt% solution of silver(I) nitrate in deionized water at 57°C for 5 minutes. After the ion-exchange bath, excess exchange solution was removed by rinsing the ion-exchanged patterned substrate briefly in deionized water at room temperature.

The rinsed ion-exchanged patterned substrate was then placed in a conventional electroless copper plating bath (as in Example 1) for 45 minutes. At the conclusion of this bath, the pattern on the substrate had accumulated a strongly adherent layer of metallic copper. The plated molded material can be seen in **FIG. 9d**. Note that the copper plating is not present where the sample was not immersed in the baths or the resin was uncured due to the presence of air bubbles.

Example 6

A photomask was fashioned by taking an awl and poking holes in a clean paint can lid in a grid pattern with approximately one inch spacing as shown in **FIG. 10a**. This mask was placed on top of a section of 3M Scotchpar® P56 2mil thick PET film which had been coated with a composition having a 20:20:10:1 ratio by weight of SR444 (Sartomer, Exton PA), SR238 (Sartomer, Exton PA), CN2404 (Sartomer, Exton PA), and TPO-L (BASF, Charlotte NC). The composition was applied by hand using a 2.5 mil Mayer rod which should have produced an approximately 6 micron thick coating.

The coated film with photomask on top was passed through a Fusion UV Curing system model MC-6RQN which was fitted with an H-Bulb and nitrogen purge. The resulting partially cured coated web was rinsed in methyl ethyl ketone (MEK) to remove all uncured acrylate.

A portion of the patterned region of the film was then subjected to ion exchange and electroless deposition. The substrate was first rinsed in deionized water (18 megohms) at 57°C for 7 minutes to prepare the surface of the pattern for the next step. An ion-exchange was then performed by bathing the patterned substrate in a 5 wt% solution of silver(I) nitrate in deionized water at 57°C for 7 minutes. After the ion-exchange bath, excess exchange solution was removed by rinsing the ion-exchanged patterned substrate briefly in deionized water at room temperature.

The rinsed ion-exchanged patterned substrate was then placed in a conventional electroless copper plating bath (as in Example 1) for 75 minutes. At the conclusion of this bath, the pattern on the substrate had accumulated a strongly adherent layer of metallic copper. **FIG. 10b** shows an image of the resulting plated dots. Note that the “dots” actually have lobes as a result of the pulsed nature of the H-bulb. Also, the cured region was much larger than the hole in the mask as a result of the diffraction of light.

While the disclosure has been particularly shown and described with reference to various embodiments thereof, it will be understood by those skilled in the art that various other changes in the form and details may be made therein without departing from the spirit and scope of the disclosure.

Thus, embodiments of a method of patterning a substrate are disclosed. One skilled in the art will appreciate that the present disclosure can be practiced with embodiments other than those disclosed. The disclosed embodiments are presented for purposes of illustration and not limitation, and the present disclosure is limited only by the claims that follow.

What is claimed is:

1. A method of patterning a substrate, comprising:

applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate; and

performing ion-exchange between the ionizable substituent and an ionic species.

2. A method according to claim 1 wherein the organic composition is a liquid and the method further comprises solidifying the organic composition to make it adhere to the substrate.

3. A method according to claim 2 wherein the organic composition comprises a solvent and the solidification comprises evaporating the solvent.

4. A method according to claim 2 wherein the organic composition comprises organic monomers, organic oligomers or mixtures thereof, and the solidification comprises initiating polymerization of the organic composition.

5. A method according to claim 4 wherein the polymerization is initiated with radiation.

6. A method according to claim 1 further comprising rinsing the patterned substrate prior to performing the ion-exchange.

7. A method according to claim 6 wherein the rinsing the patterned substrate prior to performing the ion-exchange is done in deionized water.

8. A method according to claim 6 wherein the deionized water is at a temperature above 55 degrees C.

9. A method according to claim 6 wherein the rinsing the patterned substrate prior to performing the ion-exchange is done in an aqueous base followed by rinsing in deionized water.

10. A method according to claim 9 wherein the aqueous base is a solution of ammonia hydroxide.

11. A method according to claim 9 wherein the aqueous base is a solution of sodium hydroxide.

12. A method according to claim 1 further comprising rinsing the patterned substrate after performing the ion-exchange.

13. A method according to claim 1 further comprising performing electroless plating upon the ion-exchanged substrate.

14. A method according to claim 13 further comprising reducing the ion-exchanged metal ions.

15. A method according to claim 14 wherein the reducing of the ion-exchanged metal ions is selected from the group consisting of photoreduction, chemical reduction, heat reduction, and e-beam reduction.

16. A method according to claim 13 wherein the electroless plating deposits a layer selected from the group consisting of copper, silver, nickel, gold, platinum, and palladium.

17. A method according to claim 1 wherein the metal salt is selected from the group consisting of copper, silver, nickel, gold, platinum, and palladium.

18. A method according to claim 1 wherein the metal salt is silver.

19. A method according to claim 1 wherein the organic composition comprises compounds selected from the group consisting of acrylate monomers and oligomers.

20. A method according to claim 19 wherein the organic composition comprises zinc diacrylates.

21. A method a according to claim 1 wherein the applying an organic composition having an ionizable substituent in a predetermined pattern is accomplished by a method selected from the group consisting of stamping, jet printing, scribing, photopatterning, molding, thermal transfer, screen printing, and adhering.

22. A method of generating a metal pattern onto a substrate, comprising:

applying a organic composition comprising zinc diacrylates in a predetermined pattern onto a substrate,

polymerizing the organic composition with UV radiation,

rinsing the polymerized organic composition with aqueous base followed by rinsing in deionized water at a temperature of at least 55°C,

performing ion-exchange between the polymerized organic composition and a bath containing a silver salt,

rinsing the ion-exchanged polymerized organic composition in deionized water, and

performing electroless copper plating upon the ion-exchanged polymerized organic composition.

23. A method of patterning a substrate comprising:

applying an organic composition having an ionizable substituent in a predetermined pattern onto a substrate;

rinsing the patterned substrate;

performing ion-exchange between the ionizable substituent and an ionic species;

rinsing the ion-exchanged substrate;

performing electroless deposition on the ion-exchanged substrate; and

rinsing the substrate.

24. A method of patterning a substrate comprising:

applying a radiation curable organic composition to a substrate;

curing at least a portion of the organic composition;
removing the uncured portion to form a pattern of a cured organic composition; and
performing ion-exchange to replace the ionizable substituent with an ionic species.

25. A method according to claim 24 wherein the organic composition is a liquid and the method further comprises solidifying the organic composition to make it adhere to the substrate.

26. A method according to claim 25 wherein the organic composition comprises a solvent and the solidification comprises evaporating the solvent.

27. A method according to claim 25 wherein the organic composition comprises organic monomers, organic oligomers or mixtures thereof, and the solidification comprises initiating polymerization of the organic composition.

28. A method according to claim 27 wherein the polymerization is initiated with radiation.

29. A method according to claim 24 further comprising rinsing the patterned substrate prior to performing the ion-exchange.

30. A method according to claim 29 wherein rinsing the patterned substrate prior to performing the ion-exchange is done in deionized water at a temperature above 55 degrees C.

31. A method according to claim 29 wherein rinsing the patterned substrate prior to performing the ion-exchange is done in an aqueous base followed by rinsing in deionized water.

32. A method according to claim 31 wherein the aqueous base is a solution of ammonia hydroxide.

33. A method according to claim 31 wherein the aqueous base is a solution of sodium hydroxide.

34. A method according to claim 24 further comprising rinsing the patterned substrate after performing the ion-exchange.

35. A method according to claim 24 further comprising performing electroless plating upon the ion-exchanged substrate.

36. A method according to claim 35 further comprising reducing the ion-exchanged metal ions.

37. A method according to claim 36 wherein the reducing of the ion-exchanged metal ions is selected from the group consisting of photoreduction, chemical reduction, heat reduction, and e-beam reduction.

38. A method according to claim 35 wherein the electroless plating deposits a layer selected from the group consisting of copper, silver, nickel, gold, platinum, and palladium.

39. A method according to claim 21 wherein the metal salt is selected from the group consisting of copper, silver, nickel, gold, platinum, and palladium.

40. A method according to claim 24 wherein the metal salt is silver.

41. A method according to claim 24 wherein the organic composition comprises compounds selected from the group consisting of acrylate monomers and oligomers.

42. A method according to claim 41 wherein the organic composition comprises zinc diacrylates.

43. A method a according to claim 24 wherein the applying a organic composition having an ionizable substituent in a predetermined pattern is accomplished by a method

selected from the group consisting of stamping, jet printing, scribing, photopatterning, molding, thermal transfer, screen printing, and adhering.

44. An article comprising:

a substrate;

a patterned organic composition; and

a patterned metallic coating,

wherein the patterned organic composition is covered with the patterned metallic coating to form overall features, and wherein the overall features have a width that is at least about 1 μm wide and at least 20 nm high.

45. The article according to claim 44, wherein the patterned metallic coating has a thickness of about 1Å or greater.

46. The article according to claim 44, wherein the substrate comprises a polymer.

47. The article according to claim 44, wherein the polymer comprises polyolefins, polyacrylates, polyamides, polycarbonates, polysulfones, polyethersulfones, and polyesters. Further examples of thermoplastic polymers include polyethylene, polypropylene, polystyrene, poly(methylmethacrylate), polycarbonate of bisphenol A, poly(vinyl chloride), poly(ethylene terephthalate) (PET), poly(ethylene naphthalate (PEN), poly(vinylidene fluoride), or combinations thereof.

48. The article according to claim 44, wherein the substrate comprises glass.

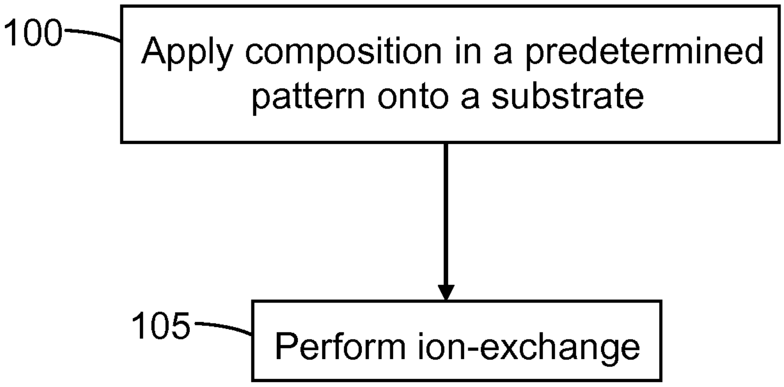
100
Apply composition in a predetermined pattern onto a substrate
105
Perform ion-exchange

Fig. 1

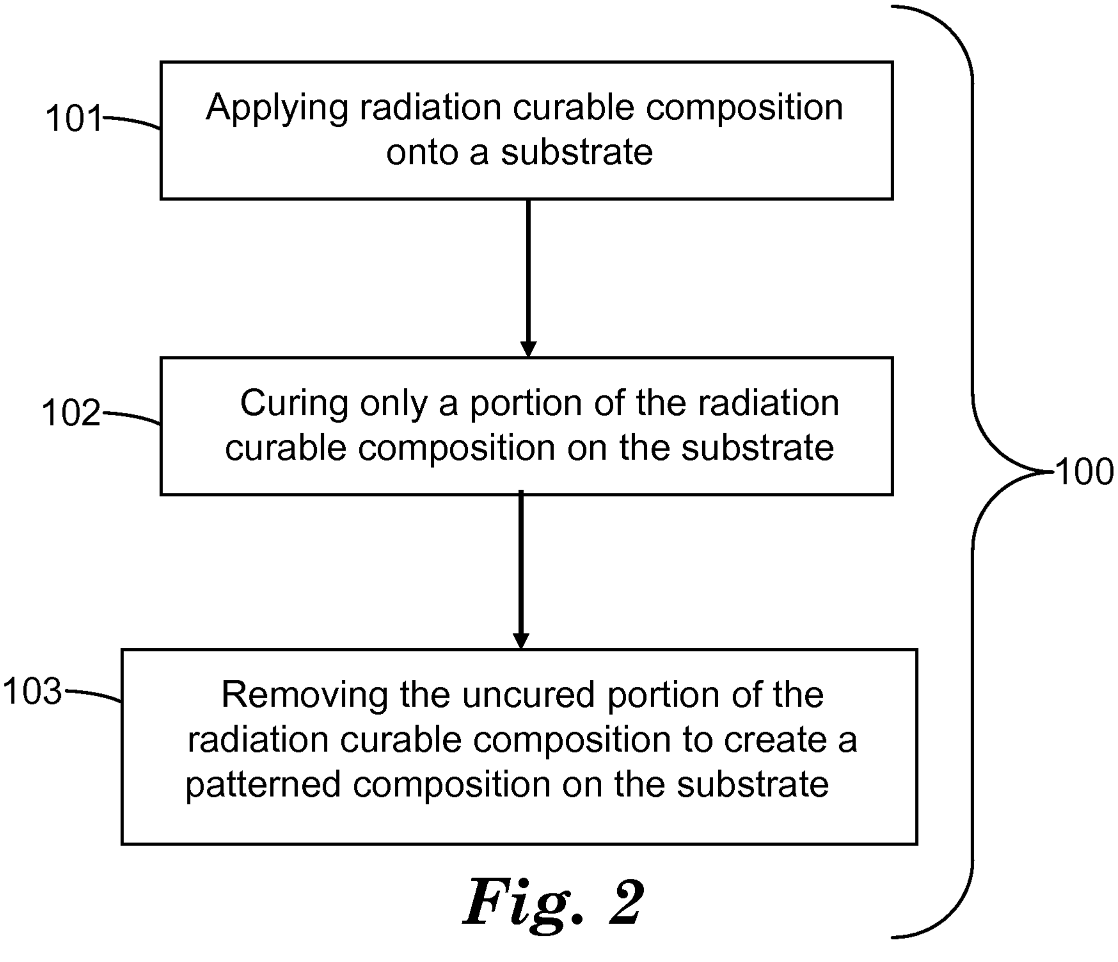
101
Applying radiation curable composition onto a substrate
102
Curing only a portion of the radiation curable composition on the substrate
103
Removing the uncured portion of the radiation curable composition to create a patterned composition on the substrate
100

Fig. 2

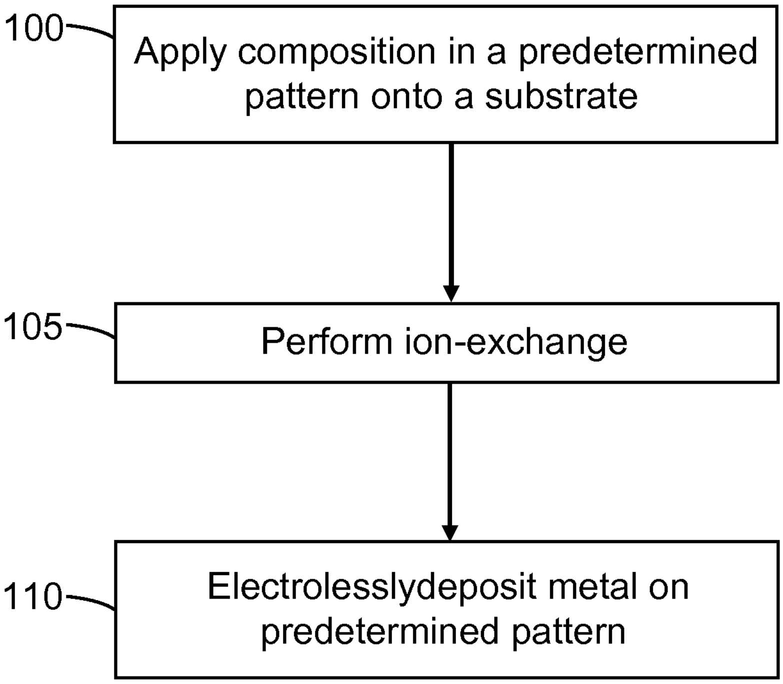
100
Apply composition in a predetermined pattern onto a substrate
105
Perform ion-exchange
110
Electrolesslydeposit metal on predetermined pattern

Fig. 3

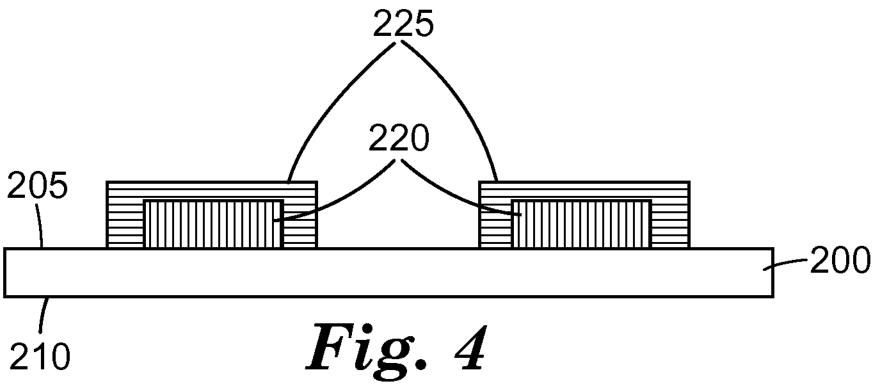
225
220
205
200
210

Fig. 4

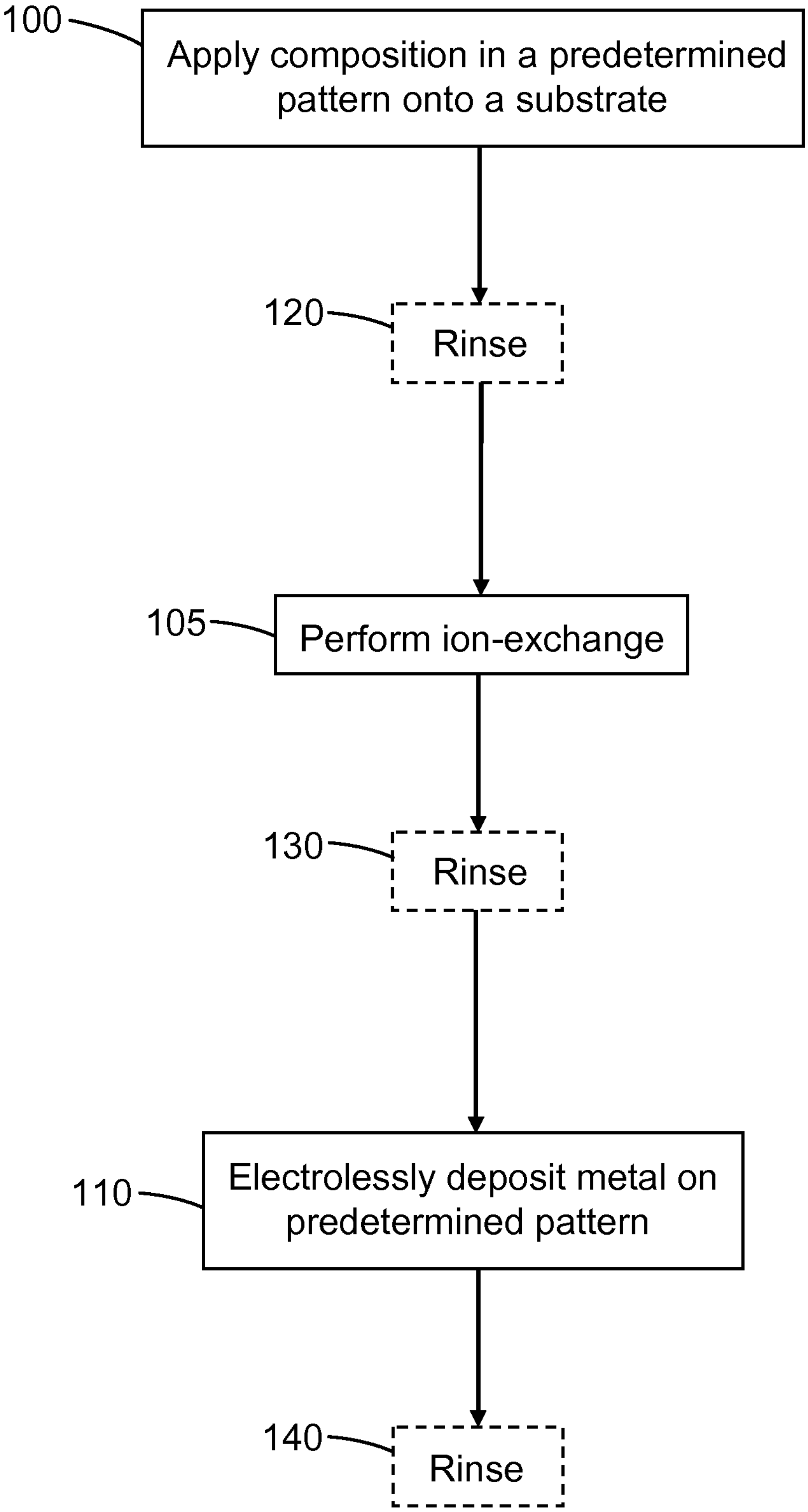
100
Apply composition in a predetermined pattern onto a substrate
120
Rinse
105
Perform ion-exchange
130
Rinse
110
Electrolessly deposit metal on predetermined pattern
140
Rinse

Fig. 5

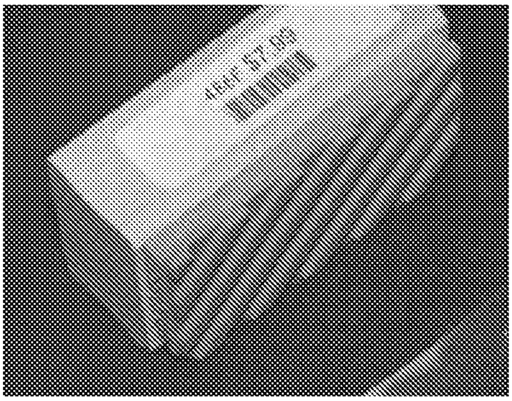

Fig. 6a

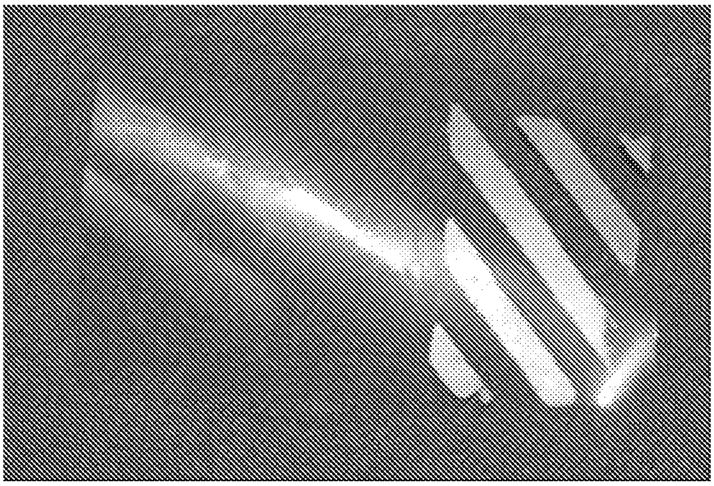

Fig. 6b

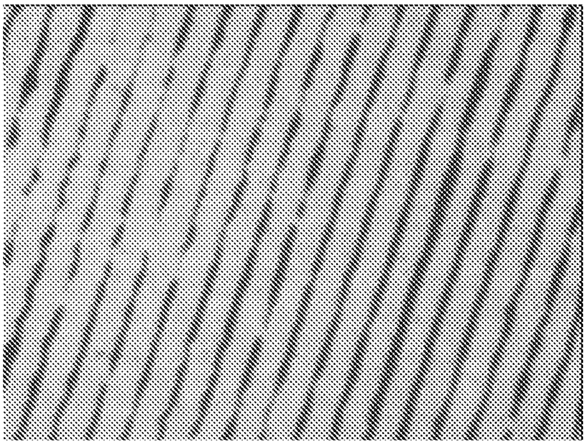

Fig. 7a

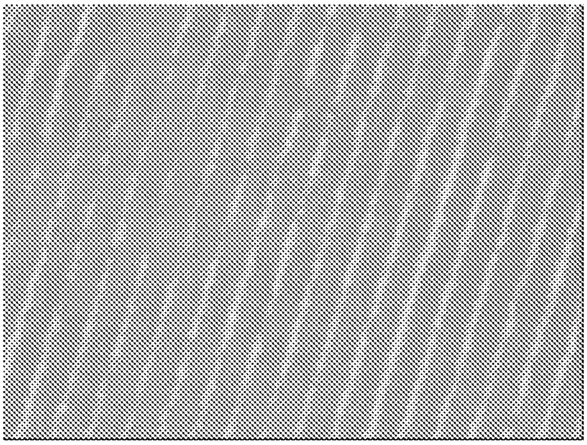

Fig. 7b

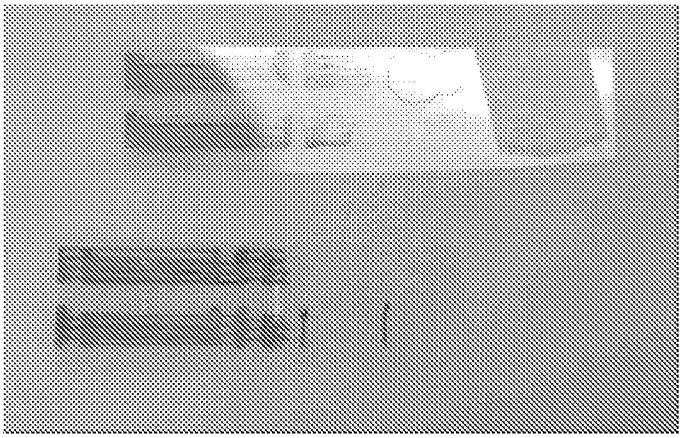

Fig. 8

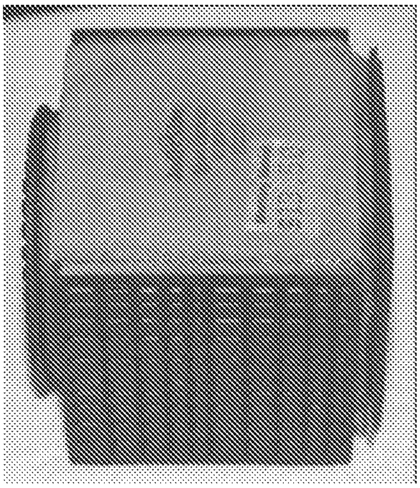

Fig. 9a

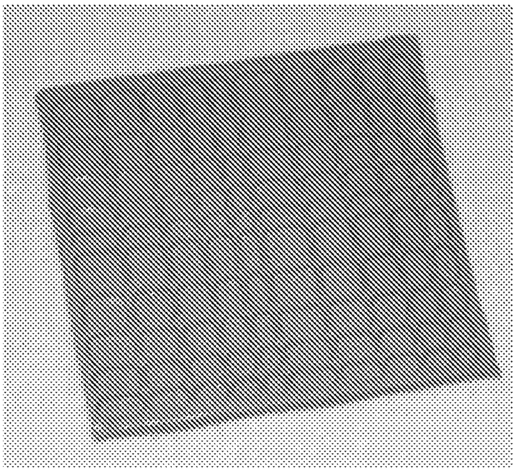

Fig. 9b

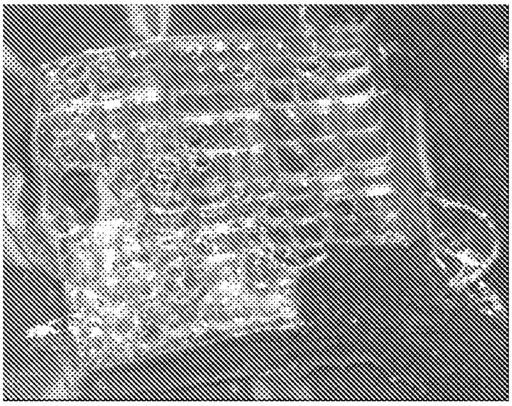

Fig. 9c

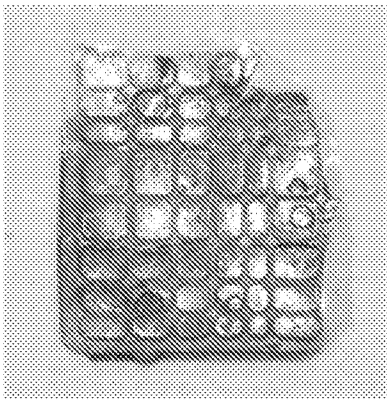

Fig. 9d

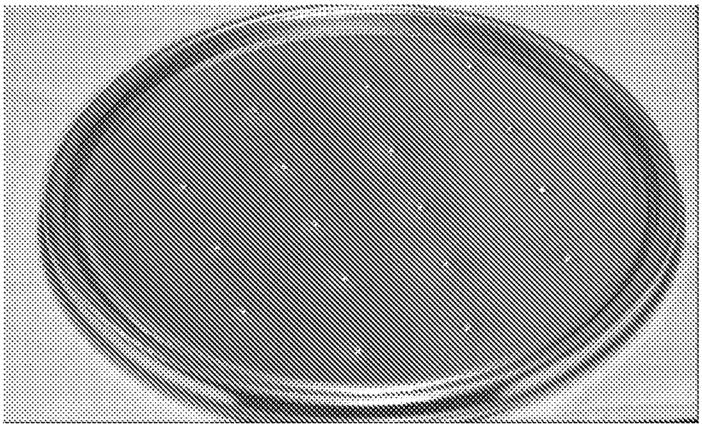

Fig. 10a

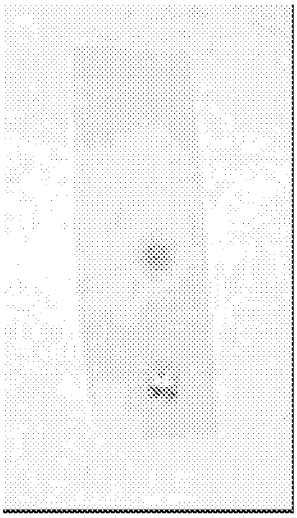

Fig. 10b