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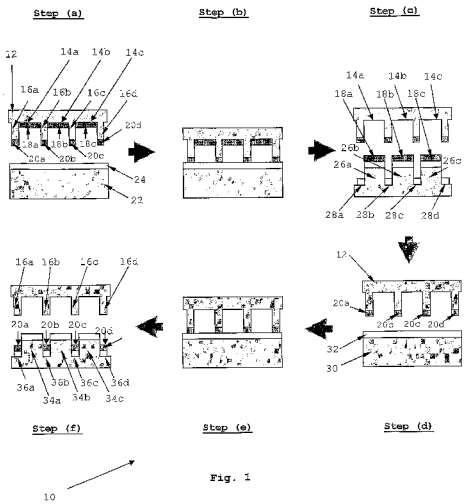
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(54) Title: A METHOD FOR FORMING METAL CAPPED SUBSTRATE IMPRINTS



(57) Abstract: A method for selectively depositing a metal layer on a substrate is provided. The method comprises the steps of:(a) providing a mold having an imprint forming surface coated with said metal layer thereon, wherein said imprint forming surface comprises a first region and a second region, and wherein said first region is dimensioned to have a greater surface area compared to said second region; and(b) contacting said mold to said substrate to form an imprint on said substrate and to simultaneously selectively deposit said metal layer from said first region of said mold to said imprint on said substrate.

A METHOD FOR FORMING METAL CAPPED SUBSTRATE IMPRINTS

Technical Field

The present invention generally relates to metal capped substrate imprints and to a method of forming imprints on a substrate that are capped with a metal layer. The capped metal imprints are useful in the reflection of light in sensors used in surface plasmon resonance.

Background

The ability to deposit or pattern various kinds of conductive materials on a substrate is an important technique in the field of electronics. Organic electronics is a branch of electronics that deals with conductive polymers. One of the key steps for the realization of advanced organic electronics is the ability to deposit or pattern various kinds of conductive materials onto a polymer substrate. Existing patterning techniques include photolithography, electron beam lithography and rigid shadow mask technology.

Conventional photolithography techniques employ light, usually in the form of ultraviolet (UV) radiation, to selectively radiate a predefined portion of a light-sensitive chemical known as photoresist, which is deposited on a substrate surface. The step of selective radiation is usually accomplished through the use of a photomask to shield/expose respective regions of the photoresist from/to the UV radiation. This process is usually followed by the partial removal of the photoresist layer and a plethora of deposition processes, such as

chemical vapor deposition (CVD) or physical vapor deposition (PVD).

A problem associated with photolithography is that selective deposition of a metal cannot be achieved without the use of a photomask or a rigid shadow mask. Furthermore, the rigid shadow mask used in the process is both expensive and time consuming to produce, thereby, increasing the capital costs associated with photolithography.

Similarly, there are also disadvantages associated with the other conventional patterning techniques. One of the disadvantages is that these conventional techniques require multiple processing steps, which in turn increases the costs involved. Another disadvantage is that these conventional techniques are either unable to selectively deposit metal on a substrate without the need of a photomask, or require extensive and elaborate alignment in order to selectively deposit a metal on a substrate. Furthermore, these techniques are unsuitable for fabrication of a metal pattern over a non-planar substrate.

With respect to sensor chips, for example those for use in surface plasmon resonance spectroscopy (SPR), previous methods of manufacturing a metal layer on such chips have been inefficient and expensive. Typically, sensor chips have relied on a Kretschmann configuration for their use. However, the Kretschmann configuration is limiting with respect to the optical properties of the support substrate and the requirement for a reflective material within a specific range. Typically this range is from 46nm to 50nm of gold. It has been previously demonstrated that the use of grating coupled surface

plasmon spectroscopy can be used wherein the substrate is coated with a reflective material, for example gold, at a thickness of about 100nm. This has enabled an increased in the efficiency at which the substrates for SPR can be made and has also lowered their cost. However, these gratings have all consisted of grating structures to which a unitary metal coating has been applied.

There is a need to provide a method of forming an imprint on a on a metal layer in which the imprint has a metal layer disposed thereon.

Summary

According to a first aspect, there is provided a method for forming an imprint on a substrate having a metal layer thereon, the method comprising the steps of:

(a) providing a mold having an imprint forming surface having a first region and a second region, said first region being dimensioned to have a greater surface area relative to said second region and wherein a metal coating is provided on said first and second regions; and

(b) forming an imprint on said first substrate by contacting said substrate with said mold, wherein said imprint forming conditions are selected such that the part of said metal coating on said first region of said mold is substantially transferred onto said formed imprint while said metal coating on said second region substantially remains on said mold.

Advantageously, due to the greater surface area on the first region of the mold as compared to that of the second region of the mold, a greater work of adhesion is generated between the first region of the mold and the corresponding region on the substrate to thereby promote

or facilitate the transfer of the metal layer onto the substrate.

Advantageously, the disclosed method may result in the formation of an imprint on the substrate as well as the deposition of a metal layer on a selected region on the imprint of the substrate at the same time.

Advantageously, it is possible to provide a reflective substrate for use in a detection system, such as an surface Plasmon resonsance system, where only a selective part, namely the micro-sized or nano-sized sized imprints, are provided with a reflective material, thereby greatly enhancing their use in the analysis of, for example, multiple biomiolecules discretely conjugated to a single sensor.

Advantageously, the disclosed method may provide a conductive pathway between a substrate comprising a polymeric bipolar plate and a catalyst of a polymeric fuel cell. Currently, the metal bipolar plate is up to 70% of the total weight of the fuel cell. This weight can be significantly reduced by using a polymeric bipolar plate with conductive material that has been applied to a selected area of the plate in accordance with the disclosed method.

Advantageously, the disclosed method may also provide control of a specific behavior of a fluid flow, using the selective metal patterning of a substrate. In particular, fluid flow can be controlled in a microfluids application.

According to a second aspect, there is provided an imprinted substrate, said substrate having a micro-sized or nano-sized imprint integrally formed on the surface thereof and having a metal layer deposited on at least part of said imprint.

According to a third aspect, there is provided a substrate having an array of micro-sized or nano-sized imprints extending from said substrate comprising a grating formation arranged to form trenches between adjacent imprints, wherein a metal layer caps one of said imprints or said trenches.

Advantageously, the formation of an imprint on the substrate and selective deposition of a metal layer onto the imprint occurs at the same time.

According to a fourth aspect, there is provided a substrate as defined above, for use in for use in a fuel cell, surface plasmon spectroscopy, organic electronics, MEMs/NEMs, a microfluidic device or a plasmonic device.

According to a fifth aspect, there is provided a substrate as defined above, wherein said substrate is obtained by the method as defined above.

According to a sixth aspect, there is provided a substrate as defined above, wherein said substrate is obtainable by the method as defined above.

According to a seventh aspect, there is provided a substrate as defined above, wherein said substrate is obtained by the method as defined above, for use in a fuel cell, surface plasmon spectroscopy, organic electronics, MEMs/NEMs, a microfluidic device or a plasmonic device.

According to a eighth aspect, there is provided a substrate as defined above, wherein said substrate is obtainable by the method as defined above for use in a fuel cell, surface plasmon spectroscopy, organic electronics, MEMs/NEMs, a microfluidic device or a plasmonic device

According to a ninth aspect, there is provided a sensor chip having a substrate body comprising an array of

micro-sized or nano-sized imprints extending from said substrate and arranged to form trenches between adjacent imprints, wherein a reflective metal layer caps one of said imprints or said trenches.

According to a tenth aspect, there is provided a surface plasmon resonance system comprising: a light source; a sensor chip as defined above; a light detector for receiving light reflected from said reflective metal layer of said sensor chip; and an optical modulator for directing modulated light onto said sensor chip.

Definitions

The following words and terms used herein shall, unless otherwise stated, have the meaning indicated:

The term "imprint" and grammatical variations thereof, in the context of this specification, is intended to cover any form of physical impression that has been made in a pliable solid body, such as a thermoplastic polymer substrate. Typically, an imprint is a generally elongate structure that extends from the surface of a substrate along a longitudinal axis extending between a proximal end disposed on or adjacent to the substrate and a distal end opposite to the proximal end. Typically, the longitudinal axis is generally normal relative to a planar axis of the substrate but the longitudinal axis may be varied significantly such as at an angle of 45° from a planar axis of the substrate. In an array of imprints that have been orderly formed as a series of rows and columns on a substrate, trenches may be formed between the adjacent rows. The imprint may be in the nano-scale or micro-scale size range both in their length dimension and

thickness dimension, and hence the trenches may also be in the nano-scale or micro-scale size range. Unless stated otherwise, in the context of this specification, the term "surface area", when referring to the first region and/or second region of the imprint forming surface of a mold is to be interpreted as referring to that part of the mold which has a metal layer that is contactable with a substrate to be imprinted. Hence, when the mold is contacted with the substrate, the term "surface area" refers to that area of the imprint forming surface of the mold that is in contact with the substrate but excludes any other areas of the mold which does not have any metal layer thereon but which may be in contact with the substrate.

The word "substantially" does not exclude "completely" e.g. a composition which is "substantially free" from Y may be completely free from Y. Where necessary, the word "substantially" may be omitted from the definition of the invention. The term "integrally formed" means that the substrate, which comprises the imprint and the metal layer is a single unitary body. Typically, the integrally formed substrate may be made in an imprint stamping method in which a mold having a metal layer disposed on an imprint forming surface is applied to a substrate under conditions to form the imprint while at the same time transferring the metal layer thereon.

The term "nanoimprinting lithography" is to be interpreted broadly to include any method for printing or creating a pattern or structure on the microscale and/or nanoscale size range on the surface of a substrate by contacting a mold with the defined pattern or structure on the surface at certain temperatures and pressures.

The terms "microscale" and ""microsized" are to be used interchangeably and are to be interpreted to include any dimensions that are in the range of about 1 (μm) to about 100 μm.

The term "nanoscale" and ""nanosized" are to be used interchangeably and are to be interpreted to include any dimensions that are below about 1 μm.

The term "three dimensional" is to be interpreted broadly to include any structures, structural features, imprints or patterns that have both lateral variations (thickness) as well as variations with depth.

The term "glass transition temperature" (T_g) is to be interpreted to include any temperature of a polymer at which the polymer lies between the rubbery and glass states. This means that above the T_g, the polymer becomes rubbery and can undergo elastic or plastic deformation without fracture. Above this temperature, such polymers can be induced to flow under pressure. When the temperature of the polymer falls below the T_g, generally, the polymer will become inflexible and brittle such that it will break when a stress is applied to the polymer. It should be noted that the T_g is not a sharp transition temperature but a gradual transition and is subject to some variation depending on the experimental conditions (e.g., film thickness, tacticity of the polymer, and the like). The actual T_g of a polymer film will vary as a function of film thickness. The T_g will be defined herein as being the bulk glass-transition temperature of the polymer substrate. The bulk glass transition temperature is a specific value that is widely agreed upon in the literature. Glass transition temperature values of

polymers may be obtained from *PPP Handbook™* software edited by *Dr D. T. Wu, 2000.*

The expression "work of adhesion" refers to the amount of interactive force acting through a contact area between the mold and the substrate and is expressed in units of Nm^{-1}.

Unless specified otherwise, the terms "comprising" and "comprise", and grammatical variants thereof, are intended to represent "open" or "inclusive" language such that they include recited elements but also permit inclusion of additional, unrecited elements.

As used herein, the term "about", in the context of concentrations of components of the formulations, typically means +/- 5% of the stated value, more typically +/- 4% of the stated value, more typically +/- 3% of the stated value, more typically, +/- 2% of the stated value, even more typically +/- 1% of the stated value, and even more typically +/- 0.5% of the stated value.

Throughout this disclosure, certain embodiments may be disclosed in a range format. It should be understood that, in the description, the range format is merely for convenience and brevity and should not be construed as an inflexible limitation on the scope of the disclosed ranges. Accordingly, the description of a range should be considered to have specifically disclosed all the possible sub-ranges as well as individual numerical values within that range. For example, the description of a range such as from 1 to 6 should be considered to have specifically disclosed sub-ranges such as from 1 to 3, from 1 to 4, from 1 to 5, from 2 to 4, from 2 to 6, from 3 to 6 and the like, as well as individual numbers within that range, for

example, 1, 2, 3, 4, 5, and 6. This applies regardless of the breadth of the range.

Disclosure of Optional Embodiments

Exemplary, non-limiting embodiments of a method for selectively depositing a metal layer on a first substrate will now be disclosed. The method comprises the step of providing a mold having an imprint forming surface having a first region and a second region, said first region being dimensioned to have a greater surface area relative to said second region and wherein a metal coating is provided on said first and second regions. The method also comprises the step of forming an imprint on said first substrate by contacting said substrate with said mold, wherein said imprint forming conditions are selected such that the part of said metal coating on said first region of said mold is substantially transferred onto said formed imprint while said metal coating on said second region substantially remains on said mold.

The inventors have found that, by using a mold in which the imprint forming surface can be visualized as having two regions of different surface areas, the region that has a larger surface area compared to the other region selectively transfers the metal layer from the mold to the substrate when the mold is applied onto the substrate. Without being bound by theory, the inventors believe that this selective transfer or deposition of the metal layer on the substrate is due to the high work of adhesion which is generated between the region of greater surface area on the mold and the corresponding region on the substrate. Due to this high work of adhesion, the selective deposition of a metal layer on the substrate is

promoted. In comparison, the region of the mold which has a smaller surface area does not result in the high work of adhesion required for transfer of the metal and hence, the metal layer on this region of the mold is not transferred to the corresponding region of the substrate when the mold is applied to the substrate.

The surface area of the first region of the imprint forming surface may be 50% greater, preferably, 60% greater, preferably, 70% greater, preferably, 80% greater, preferably 90% greater and most preferably 95% greater than that of the second region. More preferably, the first region may be greater than the second region by at least 2 fold, or at least 5 fold, or at least 10 fold or at least 15 fold or at least 20 fold or at least 25 fold.

The mold may have an imprint forming surface provided thereon and may be patterned. The patterns may comprise holes, columns, pillars, dimples, projections, gratings or trenches. The patterns may have defined heights, widths or lengths that are in the microscale or in the nanoscale. The patterns may be in a spaced apart relationship from each other. The patterns may be three-dimensional structures.

In one embodiment, the first region may refer to the patterns that protrude from the surface of the mold such as, for example, columns, projections or gratings. The second region may refer to the patterns that do not protrude from the surface of the mold, such as, for example, holes, trenches or the mold surface itself. The first region may also refer to the mold surface itself.

In another embodiment, the first region may refer to the patterns that do not protrude from the surface of the mold, such as, for example, holes, dimples, trenches or

the mold surface itself. The second region may refer to the patterns that protrude from the surface of the mold such as, for example, columns, pillars, projections or gratings. The second region may also refer to the mold surface itself.

The patterns may be formed on the mold by a method selected from the group consisting of photolithography, deep reactive ion etching, holographic lithography, e-beam lithography, ion-beam lithography and combinations thereof.

In one embodiment, the patterns on the mold may comprise gratings and/or trenches. The gratings and/or trenches may extend along respective longitudinal axes of the mold. The width of the gratings and/or trenches may be in the microscale or nanoscale. When both gratings and trenches are present on the mold, the gratings and trenches may be placed parallel to each other. The patterns on the mold may also comprise line and space patterns.

The width of the gratings and/or trenches may be independently selected from the group consisting of about 5 microns to about 50 microns, about 5 microns to about 40 microns, about 5 microns to about 30 microns, about 5 microns to about 20 microns, about 5 microns to about 10 microns, about 10 microns to about 50 microns, about 20 microns to about 50 microns, about 30 microns to about 50 microns and about 40 microns to about 50 microns. In one embodiment, the width of the gratings and corresponding channels may be about 10 microns.

The grating formation may have a grating constant in the range of 100nm to 1000nm.

The height of the grating formation may be in the range of 10 to 100nm.

The grating formation may have a shape, when viewed in cross-section, selected from the group consisting of sinusoidal wave shape, square wave, trapezoidal shape, blazed shape and triangular shape.

The gratings and/or trenches may have an aspect ratio selected from the group consisting of about 0.1 to about 3.0, about 0.1 to about 2.5,about 0.1 to about 2.0, about 0.1 to about 1.5, about 0.1 to about 1.0, and about 0.1 to about 0.5. In one embodiment, the aspect ratio of the gratings and/or trenches may be about 0.5.

In another embodiment, the patterns on the mold may comprise columns and/or circular holes. The diameter of the columns and/or circular holes may be in the microscale. The patterns on the mold may also comprise pillars and/or dimples.

The diameter of the columns and/or circular holes may be independently selected from the group consisting of about 1 micron to about 10 microns, about 1 micron to about 8 microns, about 1 micron to about 6 microns, about 1 micron to about 4 microns, about 1 micron to about 2 microns, about 2 microns to about 10 microns, about 4 microns to about 10 microns, about 6 microns to about 10 microns, about 8 microns to about 10 microns and about 4 microns to about 6 microns. In one embodiment, the diameter of the columns and/or circular holes may be about 5 microns.

The columns, pillars, dimples and/or circular holes may have an aspect ratio selected from the group consisting of about 0.1 to about 2.0, about 0.1 to about 1.5, about 0.1 to about 1.0, and about 0.1 to about 0.5.

In one embodiment, the aspect ratio of the columns, pillars, dimples and/or circular holes may be about 0.5. In another embodiment, the aspect ration of the columns, pillars, dimples and/or circular holes may be about 1.0.

The metal in the metal layer may be a metal selected from the group consisting of Group IB and Group IIIA of the Periodic Table of Elements, as well as their alloys and combinations thereof.

In one embodiment, the metal may be a metal selected from the group consisting of aluminum, copper, gold, silver, nickel and chrome and combinations thereof.

In one embodiment, the metal is gold. In another embodiment, the metal is silver.

The metal may be deposited on the surface of the mold by thermal evaporation, electron beam evaporation or sputtering.

The thickness of the metal layer on the surface of the mold may be in the range selected from the group consisting of about 50 nm to about 500 nm, about 50 nm to about 400 nm, about 50 nm to about 300 nm, about 50 nm to about 200 nm, about 50 nm to about 100 nm, about 100 nm to about 500 nm, about 200 nm to about 500 nm, about 300 nm to about 500nm and about 400 nm to about 500nm. In one embodiment, the thickness of the metal layer may be selected from the range of about 100 nm to about 200 nm.

The metal layer may be selectively deposited or transferred to the imprint of the substrate during the contacting step.

After the mold has been applied to a first substrate, the remaining metal layer that is not selectively transferred to the first substrate remains on the second region of the mold. The remaining metal layer on the

second region of the mold may be selectively transferred to a second substrate by contacting the mold to the second substrate in order to simultaneously form an imprint and to selectively deposit the metal layer from the second region of the mold to the second substrate. It will be appreciated, by those of skill in the relevant art, that the first and second contacting steps are interchangeable.

The first and/or second substrates may be a polymer substrate such as a thermoplastic polymer substrate.

The thermoplastic polymer substrate may comprise at least one monomer selected from the group consisting of acrylates, phthalamides, acrylonitriles, cellulosics, styrenes, alkyls, alkyl methacrylates, alkenes, halogenated alkenes, amides, imides, aryletherketones, butadienes, ketones, esters, acetals, carbonates and combinations thereof.

In one embodiment, the thermoplastic polymer is a polycarbonate. Exemplary monomers to form the thermoplastic polymer may be selected from the group consisting of methyls, ethylenes, propylenes, methyl methacrylates, methylpentenes, vinylidene, vinylidene chloride, etherimides, ethylenechlorinates, urethanes, ethylene vinyl alcohols, fluoroplastics, carbonates, acrylonitrile-butadiene-styrenes, etheretherketones, ionomers, butylenes, phenylene oxides, sulphones, ethersulphones, phenylene sulphides, elastomers, ethylene terephthalate, naphthalene terephthalate, ethylene naphthalene and combinations thereof.

During each of the contacting steps, the resultant imprint patterns on the substrate are of complementary configuration to those on the mold. For example, if the pattern on the mold comprises gratings, the gratings may

result in channels of complementary configuration on the respective substrate when the mold is applied to the substrate.

In one embodiment, during the step of contacting the mold to the first and/or second polymer substrate, the method may comprise the step of selecting a temperature that is above the glass transition temperature (Tg) of the first and/or second polymer substrate. At this temperature, the polymer softens and may conform to the shape of the mold such that an imprint is created on the surface of the polymer whereby the pattern of the imprint may be of complementary configuration to the pattern on the mold when the polymer is cooled and subsequently hardens. Furthermore, the mold may be preferably applied at a predetermined pressure for a certain period of time to form an imprint on the surface of the polymer substrate. The temperature and pressure to be applied will be dependent on the polymer used.

The method may comprise the use of nanoimprinting lithography. The method may result in changing the texture or three-dimensional structure of a surface of a substrate.

The molds may be made of any suitable material that is chemically inert and may be harder than the softened substrate when used at the temperature that is above the glass transition temperature of the substrate. The molds may be made of silicon, a metal, a glass, quartz, a ceramic or a combination thereof.

The temperature used when contacting the mold to a surface of the first and/or second polymer substrate may be independently selected from the group consisting of about 120°C to about 200°C, about 140°C to about 200°C,

about 160°C to about 200°C, about 180°C to about 200°C, about 120°C to about 140°C, about 120°C to about 160°C and about 120°C to about 180°C.

The temperature selected is preferably a temperature greater than that of the glass transition temperature of the first and/or second polymer substrate. Preferably, the temperature selected is approximately at least 20°C greater than the glass transition temperature of the first and/or second polymer substrate.

The pressure used when contacting the mold to a surface of the first and/or second polymer substrate may be independently selected from the group consisting of about 10 bar (1 MPa) to about 50 bar (5 MPa), about 10 bar (1 MPa) to about 40 bar (4 MPa), about 10 bar (1 MPa) to about 30 bar (3 MPa), about 10 bar (1 MPa) to about 20 bar (2 MPa), about 20 bar (2 MPa) to about 50 bar (5 MPa), about 30 bar (3 MPa) to about 50 bar (5 MPa), about 40 bar (4 MPa) to about 50 bar (5 MPa) and about 20 bar (2 MPa) to about 30 bar (3 MPa). In one embodiment, the pressure used is about 22 bar (2.2 MPa)

The time period used when contacting the mold to a surface of the first and/or second polymer substrate may be independently selected from the range of about 5 minutes to 120 minutes. For a polycarbonate substrate, the time used during the first contacting step may be about 15 minutes and the time used during the second contacting step may be about 90 minutes. It is to be appreciated, by those of skill in the relevant art, that the time used during the first and/or second contacting step depends on the type of substrate used as well as on the pattern geometry and density.

The relationship with respect to the surface area and the time of the first and second contacting steps is empirical. However, without wishing to be bound to any particular empirical observations, as a general rule, when the surface area of the first region is substantially 95% greater than that of the second region a period of time of, for example, 15 minutes is required. A longer period of time of, for example, 90 minutes is required for the second contacting step.

The method may comprise, before the first contacting step or second contacting step, the step of providing an adhesion promoter on said first substrate and said second substrate. Preferably, the adhesion promoter is applied as a surface coating on each of the first and second substrates. The adhesion promoter may aid to increase the adhesion of the metal layer to the first and/or second substrate after the metal has been selectively transferred from the mold to the first and/or second substrate. The adhesion promoter may be a silane-containing compound.

The silane-containing compound may be selected from the group consisting of 2-mercaptoethyl trimethoxysilane, 3-mercaptopropyl trimethoxysilane, 2-mercaptopropyl triethoxysilane, 3-mercaptopropyl triethoxysilane,2-mercaptoethyl tripropoxysilane, 2-mercaptoethyl tri sec-butoxysilane, 3-mercaptopropyl tri-t-butoxysilane, 3-mercaptopropyl triisopropoxysilane, 3-mercaptopropyl trioctoxysilane, 2-mercaptoethyl tri-2'-ethylhexoxysilane, 2-mercaptoethyl dimethoxyethoxysilane, 3-mercaptopropyl methoxyethoxypropoxysilane, 3-mercaptopropyl dimethoxy methylsilane, 3-mercaptopropyl methoxy dimethylsilane, 3-mercaptopropyl ethoxy dimethylsilane, 3-mercaptopropyl diethoxy methylsilane, 3-mercaptopropyl

cyclohexoxydimethyl silane, 4-mercaptobutyl trimethoxysilane, 3-mercapto-3-methylpropyltrimethoxysilane, 3-mercapto-3-methylpropyl-tripropoxysilane, 3-mercapto-3-ethylpropyl-dimethoxy methylsilane, 3-mercapto-2-methylpropyl trimethoxysilane,3-mercapto-2-methylpropyl dimethoxy phenylsilane, 3-mercaptocyclohexyl-trimethoxysilane, 12-mercaptododecyl trimethoxy silane, 12-mercaptododecyl triethoxy silane, 18-mercaptooctadecyl trimethoxysilane, 18-mercaptooctadecyl methoxydimethylsilane,2-mercapto-2-methylethyl-tripropoxysilane, 2-mercapto-2-methylethyl-trioctoxysilane, 2-mercaptophenyl trimethoxysilane, 2-mercaptophenyl triethoxysilane, 2-mercaptotolyl trimethoxysilane, 2-mercaptotolyl triethoxysilane, 1-mercaptomethyltolyltrimethoxysilane, 1-mercaptomethyltolyl triethoxysilane, 2-mercaptoethylphenyl trimethoxysilane, 2-mercaptoethylphenyl triethoxysilane, 2-mercaptoethyltolyl trimethoxysilane, 2-mercaptoethyltolyl triethoxysilane, 3-mercaptopropylphenyl trimethoxysilaneand, 3-mercaptopropylphenyl triethoxysilane, and the aminosilanes 3-aminopropyltrimethoxysilane, 3-aminopropyltriethoxysilane, 4-aminobutyltriethoxy-silane, N-methyl-3-amino-2-methylpropyltrimethoxysilane, N-ethyl-3-amino-2-methylpropyltrimethoxysilane,N-ethyl-3-amino-2-methylpropyldiethoxymethylsilane, N-ethyl-3-amino-2-methylpropyltriethoxysilane, N-ethyl-3-amino-2-methylpropyl-methyldimethoxysilane, N-butyl-3-amino-2-methylpropyltrimethoxysilane,3-(N-methyl-2-amino-1-methyl-1-ethoxy)-propyltrimethoxysilane, N-ethyl-4-amino-3,3-dimethylbutyldimethoxymethylsilane, N-ethyl-4-amino-3,3-dimethylbutyltrimethoxy-silane, N-(cyclohexyl)-3-

aminopropyltrimethoxysilane,N-(2-aminoethyl)-3-aminopropyltrimethoxysilane, N-(2-aminoethyl)-3-aminopropyltriethoxy-silane, N-(2-aminoethyl)-3-aminopropylmethyldimethoxysilane, aminopropyltriethoxysilane, bis-(3-trimethoxysilyl-2-methylpropyl)amine and N-(3'-trimethoxysilylpropyl)-3-amino-2-methylpropyltrimethoxysilane.

In one embodiment, the silane-containing compound is 3-mercaptopropyl trimethoxysilane (MPTMS).

Without wishing to be bound by any particular theory, it is believed that MPTMS is a gold adhesion promoter due to its chemical properties, wherein the thiol groups of the compound adhere to gold and the trimethoxysilane functional groups adhere to the PC substrate.

In one embodiment the surface coating of the adhesion promoter is less than 10nm.

There is provided an imprinted substrate, said substrate having a micro-sized or nano-sized imprint integrally formed on the surface thereof and having a metal layer deposited on at least part of said imprint.

There is provided a substrate having an array of micro-sized or nano-sized imprints extending from said substrate comprising a grating formation arranged to form trenches between adjacent imprints, wherein a metal layer caps one of said imprints or said trenches.

There is provided a substrate as defined above, for use in for use in a fuel cell, surface plasmon spectroscopy, organic electronics, MEMs/NEMs, a microfluidic device or a plasmonic device.

There is provided a substrate as defined above, wherein said substrate is obtained by the method as defined above.

There is provided a substrate as defined above, wherein said substrate is obtainable by the method as defined above.

There is provided a substrate as defined above, wherein said substrate is obtained by the method as defined above, for use in a fuel cell, surface plasmon spectroscopy, organic electronics, MEMs/NEMs, a microfluidic device or a plasmonic device.

There is provided a substrate as defined above, wherein said substrate is obtainable by the method as defined above for use in a fuel cell, surface plasmon spectroscopy, organic electronics, MEMs/NEMs, a microfluidic device or a plasmonic device

There is provided a sensor chip having a substrate body comprising an array of micro-sized or nano-sized imprints extending from said substrate and arranged to form trenches between adjacent imprints, wherein a reflective metal layer caps one of said imprints or said trenches.

There is provided a surface plasmon resonance system comprising: a light source; a sensor chip as defined above; a light detector for receiving light reflected from said reflective metal layer of said sensor chip; and an optical modulator for directing modulated light onto said sensor chip.

Brief Description of Drawings

The accompanying drawings illustrate a disclosed embodiment and serve to explain the principles of the disclosed embodiment. However, it is to be understood that the drawings are designed merely for the purposes of

illustration, and are not to be construed as a definition of the limits of the invention.

Fig. 1 is a schematic diagram of a method for selectively depositing a metal layer on a first substrate and subsequently selectively depositing a metal layer on a second substrate in accordance with a disclosed embodiment.

Fig. 2 shows a scanning electron microscope (SEM) image of one embodiment of a silicon mold.

Fig. 3 shows an optical microscope image (magnification: 50x) of the silicon mold of Fig. 2 after the first simultaneous imprinting and selective deposition of a metal on a first substrate.

Figs 4a and 4b show optical microscope images (magnification: a) 50x b) 5x) of the first substrate after the first simultaneous imprinting and selective deposition of a metal from the mold of Fig. 2.

Fig. 5 and Fig. 6 respectively show the corresponding elemental mapping image and corresponding SEM image of Figs 4a and 4b.

Figs 7a and 7b show optical microscope images (magnification: a) 50x b) 20x) of the second substrate after the second simultaneous imprinting and selective deposition of a metal from the mold of Fig. 2.

Fig. 8 shows a scanning electron microscope (SEM) image of a second embodiment of a silicon mold for use in a disclosed embodiment.

Fig. 9 shows an optical microscope image (magnification: 50x) of the silicon mold of Fig. 8 after

the first simultaneous imprinting and selective deposition of a metal on a first substrate.

Figs 10a and 10b show optical microscope images (magnification: a) 50x b) 20x) of the first substrate after the first simultaneous imprinting and selective deposition of a metal from the mold of Fig. 8.

Fig. 11 and Fig. 12 respectively show the corresponding elemental mapping image and corresponding SEM image of Figs 10a and 10b.

Fig. 13 shows a scanning electron microscope (SEM) image of a third embodiment of a silicon mold for use in a disclosed embodiment.

Fig. 14 shows an optical microscope image (magnification: 50x) of the silicon mold of Fig. 13 after the first simultaneous imprinting and selective deposition of a metal on a first substrate.

Figs 15a and 15b show optical microscope images (magnification: a) 50x b) 20x) of the first substrate after the first simultaneous imprinting and selective deposition of a metal with the mold of Fig. 13.

Fig. 16 and Fig. 17 respectively show the corresponding elemental mapping image and corresponding SEM image of Figs 10a and 10b.

Figs 18a and 18b show optical microscope images (magnification: a) 50x b) 20x) of the second substrate after the second simultaneous imprinting and selective deposition of a metal from the mold of Fig. 14.

Detailed Description

Fig. 1, shows a schematic diagram of a method 10 for selectively depositing a metal layer on a first substrate (Steps (a)-(c)) and subsequently selectively depositing a metal layer on a second substrate (Steps (d)-(f)).

In Step (a) of Fig. 1, a silicon (Si) mold 12 having an imprint forming surface comprising a first region (14a, 14b, 14c) and a second region comprising projections (16a, 16b, 16c, 16d) is coated with a reflective metal, such as gold (Au), by electron beam evaporation. The mold 12 is attached inside an electron beam evaporator (not shown) at a distance from a Au target, such that the evaporation is unidirectional, resulting in a gold coating layer (18a, 18b, 18c) being formed on the first region (14a, 14b, 14c) and a gold coating layer (20a, 20b, 20c, 20d) being formed on the second region (16a, 16b, 16c, 16d). The first region (14a, 14b, 14c) has a greater surface area (250,000μm^2) compared to the second region (10,000μm^2) (16a, 16b, 16c, 16d).

Prior to Step (a), a first polycarbonate (PC) substrate 22 is treated with an adhesion promoter, (3-mercaptopropyl)trimethoxysilane (MPTMS), to form a surface coating 24 of the adhesion promoter.

In Step (b) of Fig. 1, the Si mold 12 is pressed into the surface of the PC substrate 22, at a temperature above the glass transition temperature of 180°C of the PC substrate 22, at a pressure of 2.2 MPa for 15 minutes to form an imprint on the PC substrate 22.

In Step (c) of Fig. 1, the PC substrate 22 is cooled to a temperature of 100°C for a time period of 1-5 minutes before demolding the PC substrate 22 from the Si mold 12.

The imprint formed on the PC substrate 22 comprises a first region of projections (26a, 26b, 26c) and a second region of recessed portions (28a, 28b, 28c, 28d). The gold layer (18a, 18b, 18c) on the first region (14a, 14b, 14c) of the mold 12 is transferred to the corresponding first region of projections (26a, 26b, 26c) on the PC substrate 22. This is due to the greater surface area on the first region (14a, 14b, 14c) of the mold 12 as compared to the second region of projections (16a, 16b, 16c, 16d) of the mold 12, which results in a greater work of adhesion between the first region (14a, 14b, 14c) of the mold 12 and the corresponding first region of projections (26a, 26b, 26c) formed on the PC substrate 22.

In Step (d) of Fig. 1, the same Si mold 12 with the gold coating layer (20a, 20b, 20c, 20d) on the second region of projections (16a, 16b, 16c, 16d), is used for the simultaneous imprinting and selective deposition of a metal onto a second PC substrate 30. The second PC substrate 30 is also treated with the adhesion promoter (3-mercaptopropyl)trimethoxysilane (MPTMS), to form a surface coating 32 of the adhesion promoter.

In Step (e) of Fig. 1, the Si mold 12 is pressed into the surface of the PC substrate 30, at a temperature above the glass transition temperature of 180°C of the PC substrate 30, at a pressure of 2.2 MPa for 90 minutes to form an imprint on the PC substrate 30.

In Step (f) of Fig. 1, the PC substrate 30 is cooled to a temperature of 100°C for a time period of 1-5 minutes before demolding the PC substrate 30 from the Si mold 12. The imprint formed on the PC substrate 30 comprises a first region of projections (34a, 34b, 34c) and a second region of recessed portions (36a, 36b, 36c, 36d). The gold

layer (20a, 20b, 20c, 20d) on the second region (16a, 16b, 16c, 16d) of the Si mold 12 is transferred to the corresponding second region (36a, 36b, 36c, 36d) on the PC substrate 30.

Examples

Non-limiting examples of the invention will be further described in greater detail by reference to specific Examples, which should not be construed as in any way limiting the scope of the invention.

Materials and Methods

Gold Deposition

A silicon (Si) mold was coated with gold by electron beam evaporation at a pressure of 3.8×10^{-6} mbar (3.8×10^{-7} kPa), a current of 100mA and a deposition rate of 0.11nm/s. The Si mold was attached inside an Edwards Auto 306 electron beam evaporator at a distance away from the gold target to ensure that the gold was deposited unidirectionally on the silicon mold. Gold was not deposited on the sidewalls of any recessed areas. The thickness of the gold layer was in the range of about 100nm to 200nm.

Surface Treatment of Polycarbonate

A polycarbonate (PC) film was treated with an adhesion promoter, (3-mercaptopropyl)trimethoxysilane (MPTMS), to enhance adhesion between the polycarbonate and the gold layer during the imprinting process. The polycarbonate films were soaked in a solution of 5ml MPTMS mixed with 240 ml ethanol and 10ml de-ionized water. The films were left overnight in the solution to enable the

MPTMS to react with the polycarbonate film to form a surface coating on the adhesion promoter.

Gold Transfer

Imprinting was carried out with a gold-coated silicon mold and a MPTMS-treated polymeric substrate utilizing the classic nanoimprint lithography process. The gold-coated mold was placed on top of the polymeric substrate on an *Obducat* imprinter. The heating temperature was then increased to a temperature above the glass transition temperature (180°C) of the polymeric substrate and a pressure of 22bar (2.2kPa) was applied for 15 minutes. The silicon mold was then demolded from the polymer at 100°C.

After imprinting, the gold layer was transferred from either the protruding region or the recessed region of the mold, to the corresponding recessed region or protruding region of the polymeric imprinted substrate. The region where the gold transfer occurs can be controlled by the geometric pattern of the mold. In particular, the gold transfer will occur in the region with a larger surface area compared to the other region. The surface area of the first region is approximately 95% greater than the surface area of the second region.

The remaining gold attached on the silicon mold was used for a subsequent new imprinting step. The heating temperature was again increased to a temperature above the glass transition temperature (180°C) of the polymeric substrate and a pressure of 22 bar (2.2kPa) was applied for 90 minutes. The exact imprinting time depends on the pattern geometry and density. At the end of the cycle, the silicon mold was demolded from the polymer at 100°C. After imprinting, the remaining gold layer was transferred from

the silicon mold to the polymeric substrate in the region opposite to the first imprint.

Characterization

As there was a significant difference in the reflectivity of the polymer and gold, optical microscope images were used to characterize the consistency of the selective gold transfer. In the optical microscope images, the "brighter" regions represent the regions covered with gold, whereas the "darker" regions represent the regions without gold.

Energy dispersive X-ray spectroscopy (EDS elemental mapping) was also used to validate the results obtained from the optical microscope images. Similarly, EDS elemental mapping permits a specific element such as gold to appear "brighter" at the regions covered with gold, whereas other regions without gold appear "darker".

Example 1

This example describes the method 10 as illustrated in Fig. 1 using a Si mold with a 10 μm (A/R = 0.5) pillar pattern as shown in Fig. 2. The Si mold has an imprint forming surface comprising a first recessed region 40 and a second protruding region 42 coated with gold as described above. A PC substrate was also treated with an adhesion promoter as described above.

During the first imprinting step, the gold (Au) layer in the first recessed region 40 of the Si mold was transferred to the corresponding protruding region 50 of the PC substrate (Figs 4a and 4b), whereas the gold layer on the protruding region 42 remained on the Si mold (Fig. 3). The corresponding recessed region 52 on the PC

substrate (Figs 4a and 4b), does not have a gold layer. Referring to Figs 2 and 3, the recessed region 40 of the Si mold has a larger surface area compared to the protruding region 42 of the Si mold which promotes or facilitates the transfer of the gold layer from the recessed region 40 of the Si mold onto the substrate.

EDS elemental mapping was carried out to validate the presence of gold on the substrate. Fig. 5 shows the elemental mapping image of the substrate and Fig. 6 shows the corresponding SEM image. As can be seen, the gold is present on the protruding region 50 of the PC substrate.

Subsequently, a second imprinting step was then carried out on a second substrate as described above. The remaining gold layer on the second protruding region 42 of the Si mold was transferred to the corresponding recessed region 60 of the second substrate. The protruding region 62 of the second substrate does not have a gold layer (Figs 7a and 7b).

Example 2

This example describes a method for selectively depositing a gold layer using a silicon mold with a 5 μm (A/R = 1.0) dimple pattern as shown in Fig. 8. The silicon mold has an imprint forming surface comprising a first protruding region 70 and a second recessed region 72. As shown in Figs 8 and 9, the first protruding region 70 of the Si mold has a larger surface area compared to the second recessed region 72 of the Si mold.

The silicon mold was coated with a gold layer as described above. A PC substrate was also treated with an adhesion promoter as described above.

During the first imprinting step the gold layer in the protruding region 70 was transferred to the corresponding recessed region 80 of the PC substrate (Figs 10a and 10b), whereas the gold layer on the recessed region 72 remained on the Si mold (Fig. 9). As such, the corresponding protruding region 82 on the PC substrate, as shown in Figs 10a and 10b, does not have a gold layer. The larger surface area of the protruding region 70 of the Si mold, compared to the recessed region 72 of the Si mold, promotes or facilitates the transfer of the gold layer from the protruding region 70 of the Si mold onto the substrate.

EDS elemental mapping was carried out to validate the presence of gold on the substrate. Fig. 11 shows the elemental mapping image of the substrate and Fig. 12 shows the corresponding SEM image. As can be seen, the gold is present on the recessed region 80 of the PC substrate.

Example 3

This example describes the method 10 as illustrated in Fig. 1 using a silicon mold with a 10 μm (A/R = 0.5) grating pattern as shown in Fig. 13. The silicon mold having an imprint forming surface comprising a first recessed region 90 and a second protruding region 92 was coated with gold as described above. A PC substrate was also treated with an adhesion promoter as described above.

During the first imprinting step, the gold layer in the recessed region 90 was transferred to the corresponding protruding region 100 of the PC substrate (Figs 15a and 15b), whereas the gold layer on the protruding region 92 remained on the Si mold (Fig. 14). As such, the corresponding recessed region 102 on the PC

substrate, as shown in Figs 15a and 15b, does not have a gold layer. Referring to Figs 13 and 14, the recessed region 90 of the Si mold has a larger surface area compared to the protruding region 92 of the Si mold which promotes or facilitates the transfer of the gold layer from the recessed region 90 of the Si mold onto the substrate.

EDS elemental mapping was carried out to validate the presence of gold on the substrate. Fig. 16 shows the elemental mapping image of the substrate and Fig. 17 shows the corresponding SEM image. As can be seen, the gold is present on the protruding region 100 of the PC substrate and is absent from the recessed portion 102 of the substrate.

Subsequently, a second imprinting step was then carried out on a second substrate treated as described above. The remaining gold layer on the protruding region 92 of the Si mold was transferred to the corresponding recessed region 200 of the second substrate. The protruding region 202 of the second substrate does not have a gold layer (Figs 18a and 18b).

Applications

The method disclosed herein provides a process for selectively depositing a metal layer on at least part of a substrate.

Advantageously, selective deposition of a metal onto a substrate in accordance with the disclosed method can be achieved without the use of a photomask or a rigid shadow mask.

Advantageously, the method disclosed herein is more cost effective and less time consuming than conventional

methods as the method disclosed herein avoids the need for additional equipment or processes.

Advantageously, the method disclosed herein results in the formation of an imprint on the substrate as well as the deposition of a metal layer on a selected region on the imprint of the substrate at the same time. More advantageously, the method disclosed herein is able to selectively deposit a metal layer over a non-planar substrate.

Advantageously, the use of a mold as disclosed herein can be used for subsequent imprinting of similar or different substrates. This is because the metal layer which remains on the mold during the first simultaneous imprinting and selective metal deposition may be used for a subsequent simultaneous imprinting and selective metal deposition on a further substrate.

Advantageously, the substrate according to the invention may be used in a fuel cell, surface plasmon spectroscopy, organic electronics, MEMs/NEMs, a microfluidic device or a plasmonic device.

It will be apparent that various other modifications and adaptations of the invention will be apparent to the person skilled in the art after reading the foregoing disclosure without departing from the spirit and scope of the invention and it is intended that all such modifications and adaptations come within the scope of the appended claims.

Claims

1. A method for forming an imprint on a substrate having a metal layer thereon, the method comprising the steps of:

(a) providing a mold having an imprint forming surface having a first region and a second region, said first region being dimensioned to have a greater surface area relative to said second region and wherein a metal coating is provided on said first and second regions; and

(b) forming an imprint on said first substrate by contacting said substrate with said mold, wherein said imprint forming conditions are selected such that the part of said metal coating on said first region of said mold is substantially transferred onto said formed imprint while said metal coating on said second region substantially remains on said mold.

2. The method as claimed in claim 1, wherein the imprint is a generally elongate imprint having a longitudinal axis and a proximal end that is proximal to the substrate and a distal end that is opposite to said proximal end.

3. The method as claimed in claim 2, wherein the part of said metal coating that is transferred from the first region of said mold is deposited onto the distal end of imprint.

4. The method as claimed in claim 2, wherein the part of said metal coating that is transferred from the first region of said mold is deposited onto the sidewall disposed between the distal and proximal end of the imprint.

5. The method as claimed in any one of the preceding claims, further comprising after step (b), the step of:

(c) contacting said mold to a second substrate to form an imprint on said second substrate to transfer said metal coating on said second region to said formed imprint on said second substrate.

6. The method as claimed in any one of claims 1 to 4, comprising the step of providing an adhesive layer on said substrate before said contacting step (b).

7. The method as claimed in any one of the preceding claims, wherein said first substrate and said second substrate is a thermoplastic polymer.

8. The method as claimed in claim 7, wherein said thermoplastic polymer comprises monomers selected from the group consisting of acrylates, phthalamides, acrylonitriles, cellulosics, styrenes, alkyls, alkyls methacrylates, alkenes, halogenated alkenes, amides, imides, aryletherketones, butadienes, ketones, esters, acetals, carbonates and co-monomers thereof.

9. The method as claimed in claim 7 or claim 8, comprising, during said contacting steps (b) and (c), the step of selecting a temperature that is above the glass transition temperature of said thermoplastic polymer.

10. The method as claimed in claim 9, wherein said temperature during said contacting steps (b) and (c) is at least 20°C above the glass transition temperature of said thermoplastic polymer.

11. The method as claimed in any one of claims 5 to 10, comprising, during said contacting steps (b) and (c), the step of selecting a pressure from the range of 10 Bar (1 MPa) to 50 Bar (5MPa).

12. The method as claimed in any one of claims 5 to 11, comprising, during said contacting steps (b) and (c), the step of selecting a time period from the range of 5 minutes to 120 minutes.

13. The method as claimed in any one of the preceding claims, comprising the step of selecting the metal of said metal layer from at least one of Group IB and Group IIIA of the Periodic Table of Elements.

14. The method as claimed in any one of the preceding claims, comprising the step of selecting the surface area of said first region on said imprint forming surface as 95% greater than the area of said second region.

15. The method as claimed in any one of claims 6-14, comprising the step of selecting a layer of a silane-containing compound as said adhesive layer.

16. An imprinted substrate, said substrate having a micro-sized or nano-sized imprint integrally formed on the surface thereof and having a metal layer deposited on at least part of said imprint.

17. A substrate having an array of micro-sized or nano-sized imprints extending from said substrate comprising a grating formation arranged to form trenches

between adjacent imprints, wherein a metal layer caps one of said imprints or said trenches.

18. A substrate according to claim 16 or claim 17, wherein the metal layer caps only one of said imprints or said trenches but not both.

19. A substrate according to claim 16 or claim 17, wherein each of said imprints are individually capped by the metal layer while the trenches are not capped by the metal layer.

20. A substrate according to claim 16 or claim 17, wherein an adhesive layer may be disposed between the imprints and the metal layer.

21. A substrate according to claim 16 or claim 17, wherein the trenches are individually capped by the metal layer while the imprints are not capped.

22. A substrate according to claim 16 or claim 17, wherein, an adhesive layer may be disposed between the metal layer and the base of the trenches.

23. The substrate as claimed in claim 16, wherein said imprint comprises a plurality of trenches, gratings, columns and circular holes.

24. The substrate as claimed in claim 23, wherein the dimensions of said trenches, gratings, columns and circular holes are independently selected from the microscale or nanoscale.

25. The substrate as claimed in any one of claims 16 to 24, wherein said substrate is a thermoplastic polymer.

26. The substrate as claimed in claim 25, wherein said thermoplastic polymer is polycarbonate.

27. The substrate as claimed in any one of claims 16-26, wherein the metal of said metal layer is selected from at least one of Group IB and Group IIIA of the Periodic Table of Elements

28. The substrate as claimed in claim 27, wherein said metal is selected from the group consisting of aluminum, copper, gold, silver and combinations thereof.

29. The substrate as claimed in any one of claims 20-28, wherein said adhesive layer is a layer comprising silane-containing compounds.

30. A substrate according to claim 17, wherein said said grating formation has a grating constant in the range of 100nm to 1000nm.

31. A substrate according to claim 30, wherein the height of said grating formations is in the range of 10 to 100nm.

32. A substrate according to claim 30 or 31, wherein said grating formation has a shape, when viewed in cross-section, selected from the group consisting of sinusoidal wave shape, square wave, trapezoidal shape, blazed shape and triangular shape.

33. Use of a substrate according to any one of claims 16 to 32, in a fuel cell, surface plasmon spectroscopy, organic electronics, MEMs/NEMs, a microfluidic device or a plasmonic device.

34. A substrate according to any one of claims 16-32, wherein said substrate made in the method according to any one of claims 1 to 15.

35. A sensor chip having a substrate body comprising an array of micro-sized or nano-sized imprints extending from said substrate and arranged to form trenches between adjacent imprints, wherein a reflective metal layer caps one of said imprints or said trenches.

36. A surface Plasmon resonance system comprising:

a light source;

a sensor chip as claimed in claim 35;

a light detector for receiving light reflected from said reflective metal layer of said sensor chip; and

an optical modulator for directing modulated light onto said sensor chip.

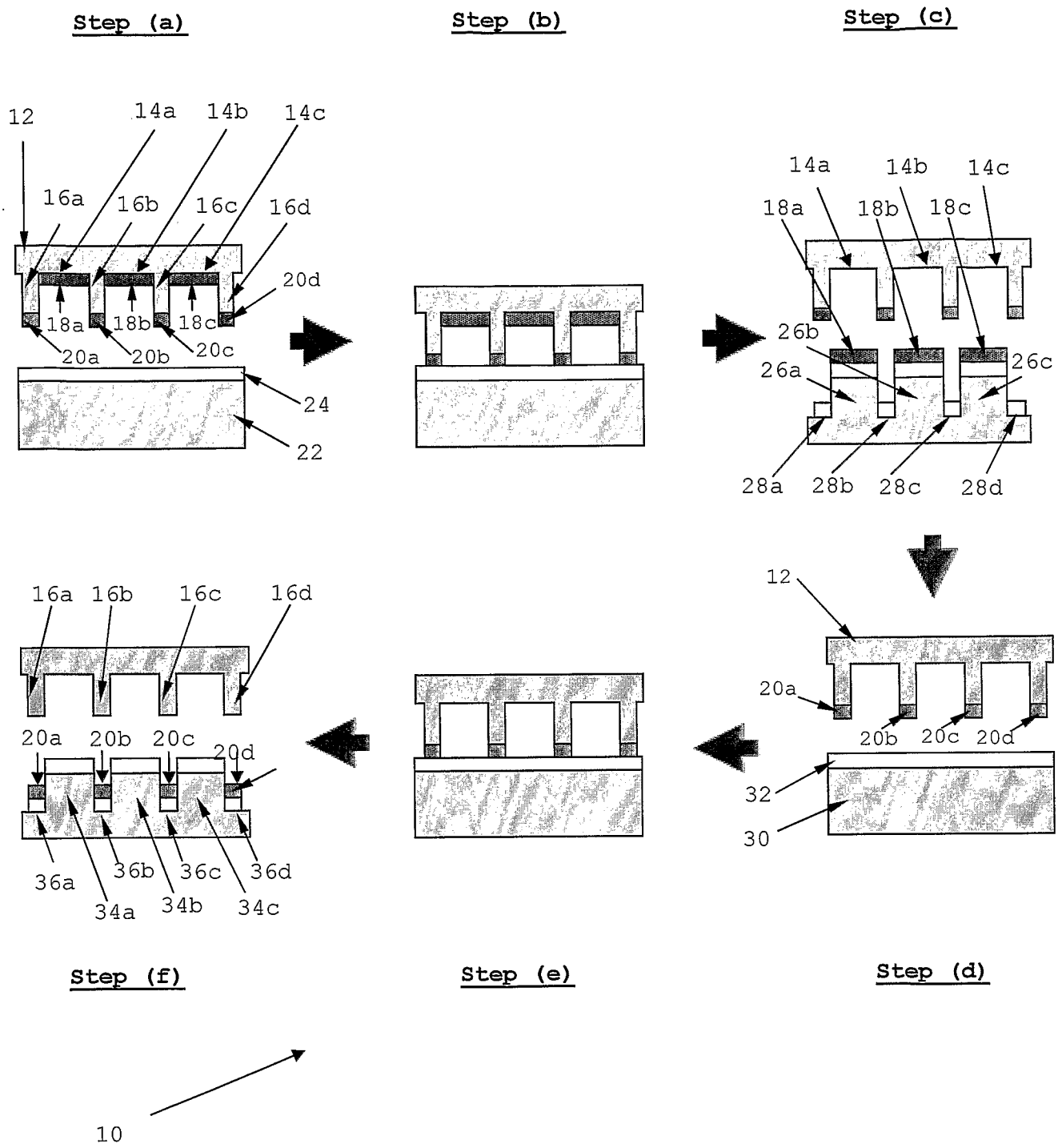

Step (a)
Step (b)
Step (c)
12
14a
14b
14c
16a
16b
16c
16d
18a
18b
18c
20d
20a
20b
20c
24
22
26a
26b
26c
28a
28b
28c
28d
Step (d)
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Step (f)
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34b
34c
10

Fig. 1

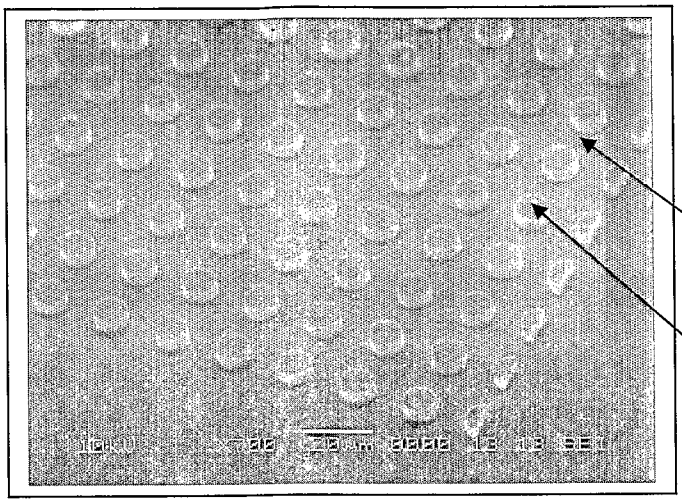


Fig. 2

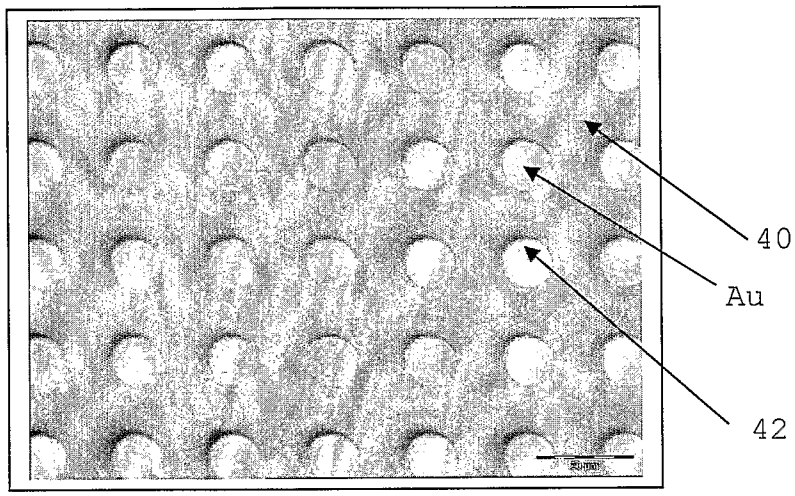


Fig. 3

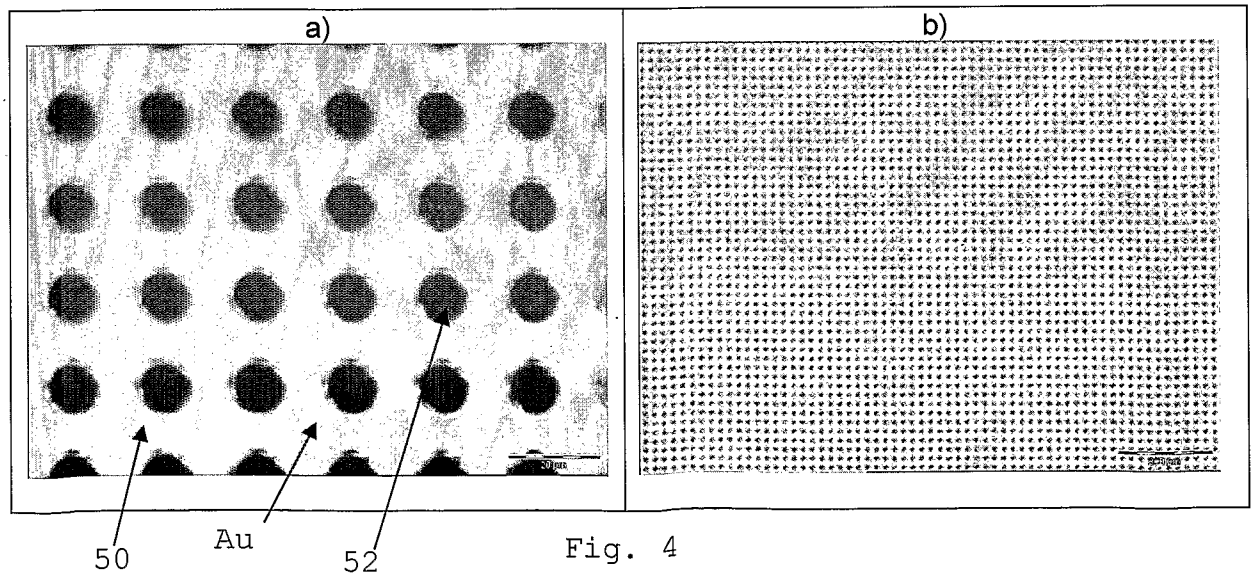


Fig. 4

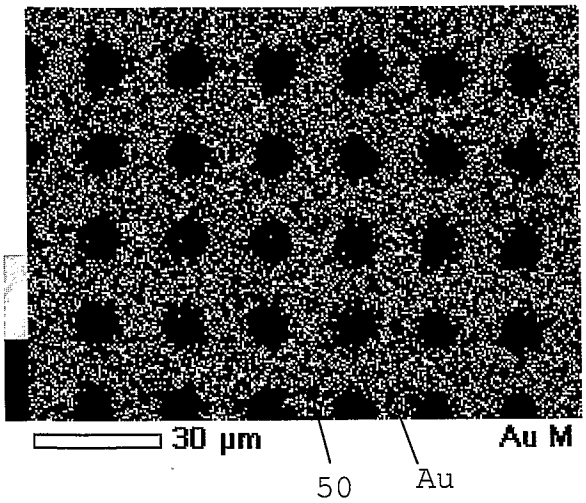


Fig. 5

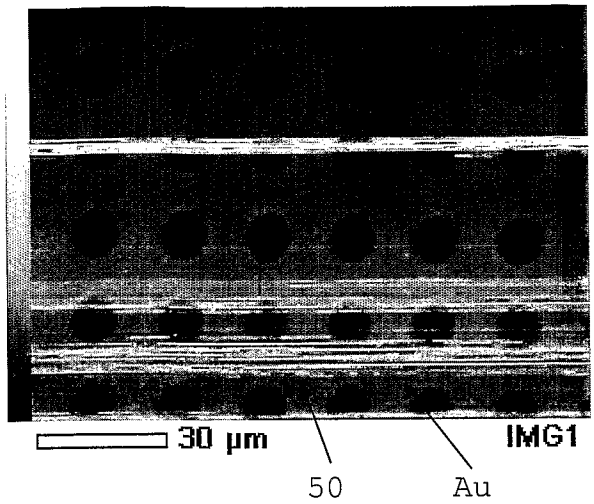


Fig. 6

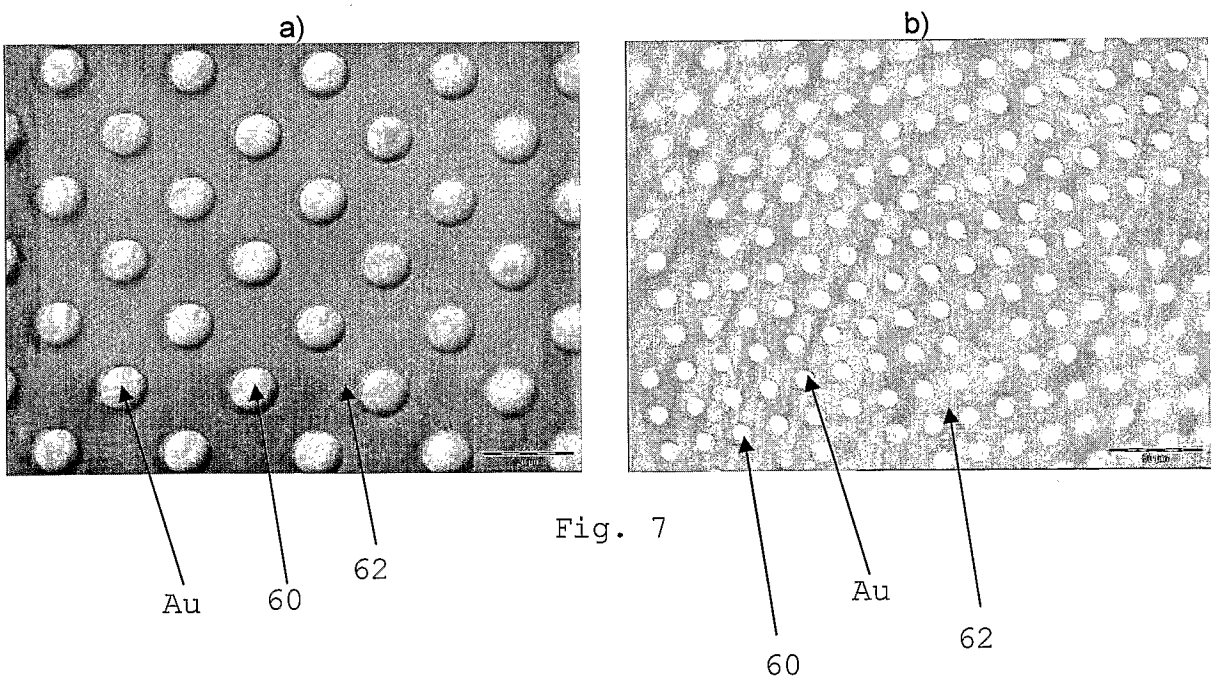


Fig. 7

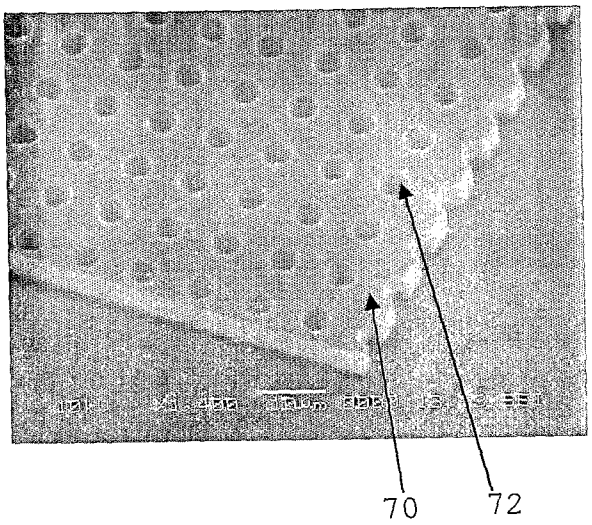


Fig. 8

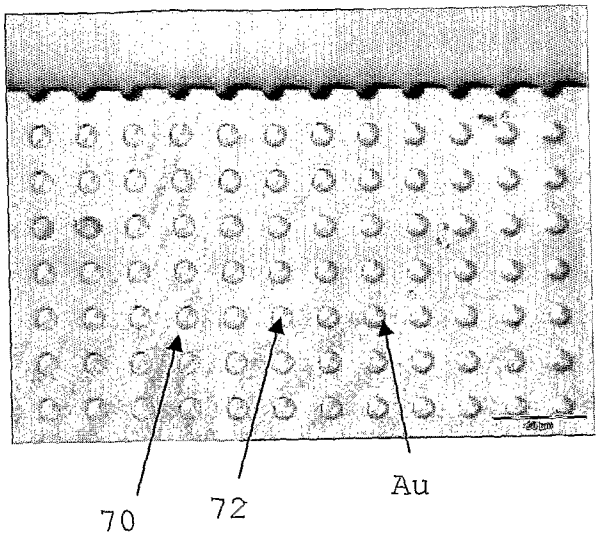


Fig. 9

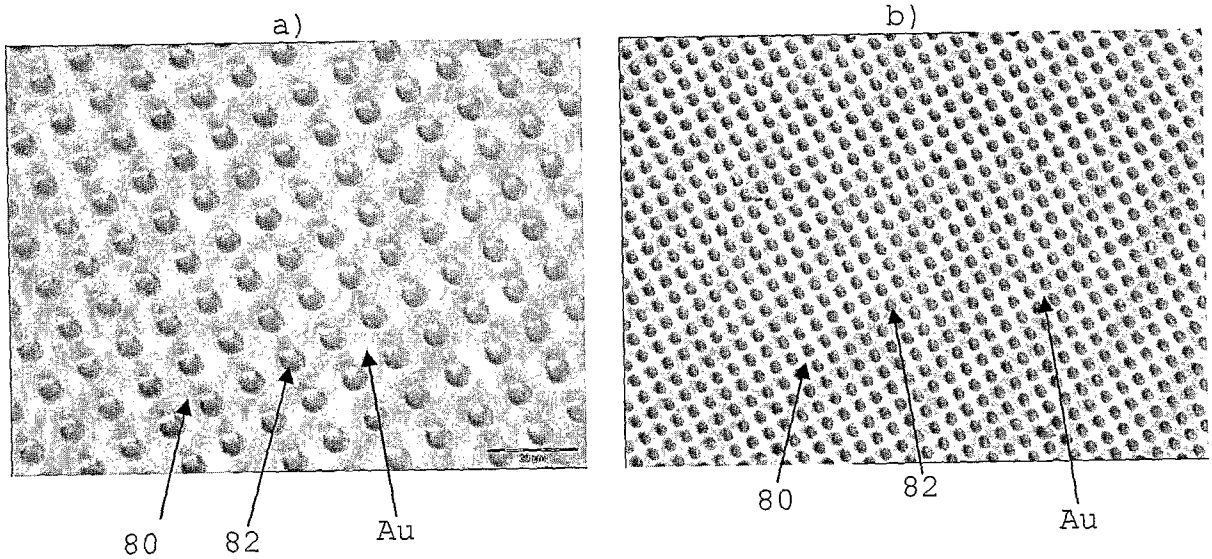


Fig. 10

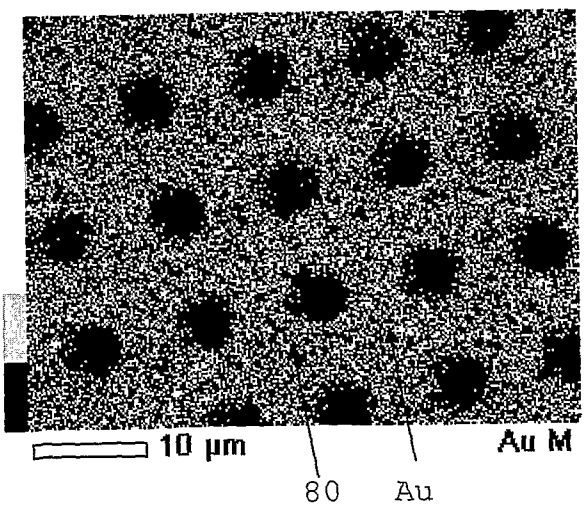


Fig. 11

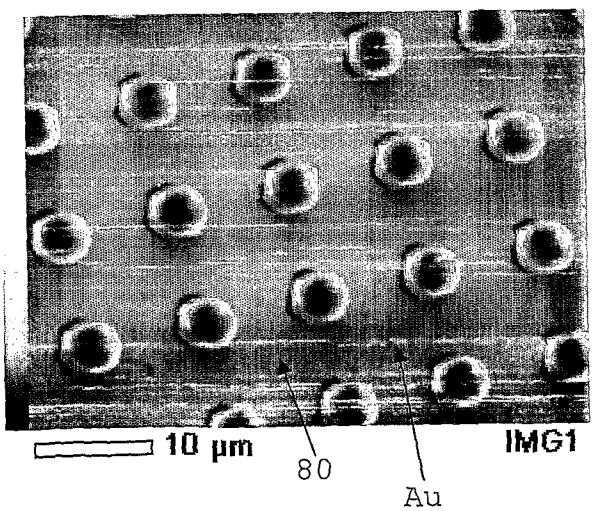


Fig. 12

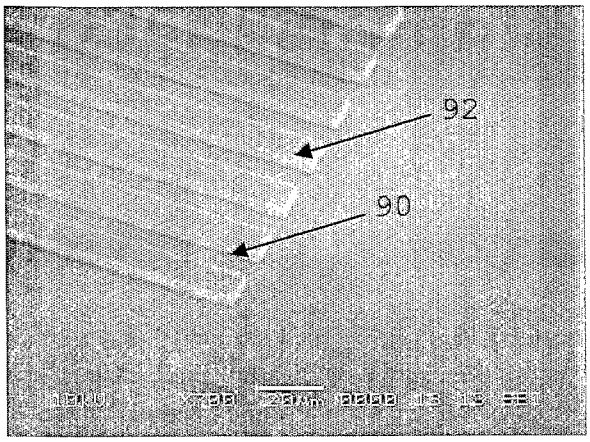


Fig. 13

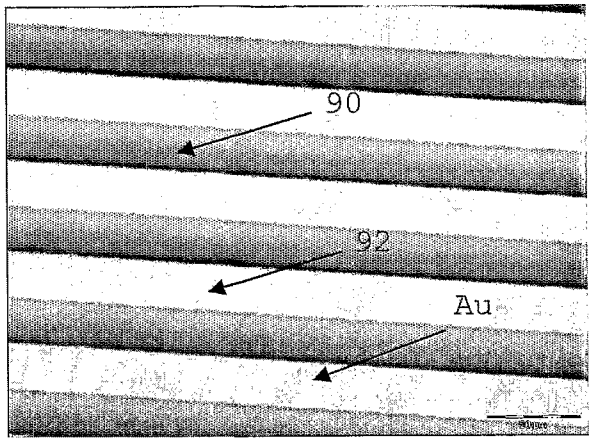


Fig. 14

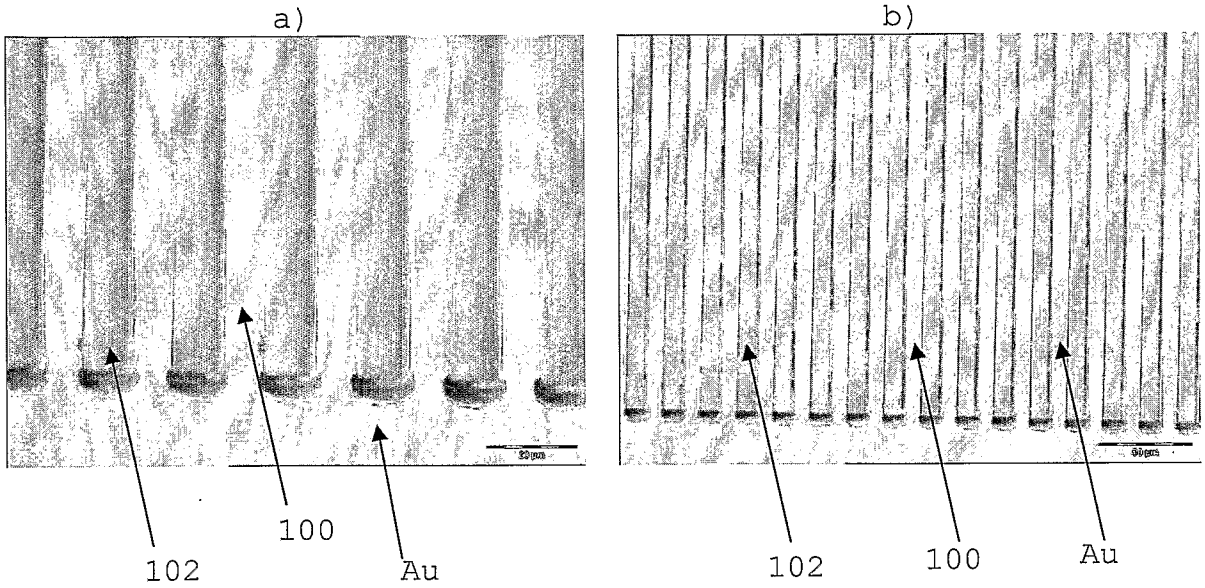


Fig. 15

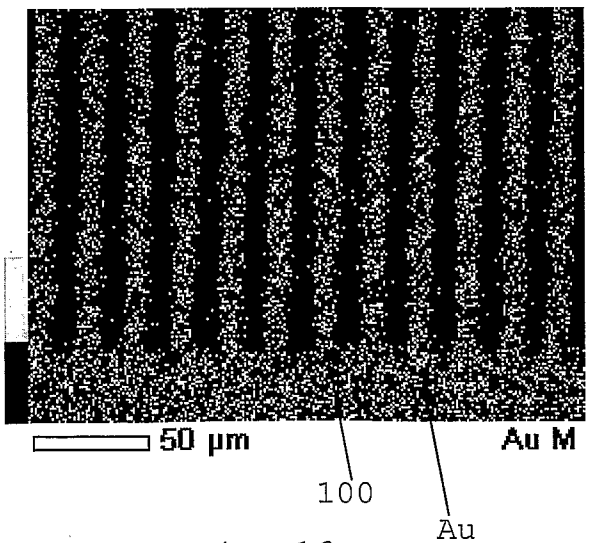


Fig. 16

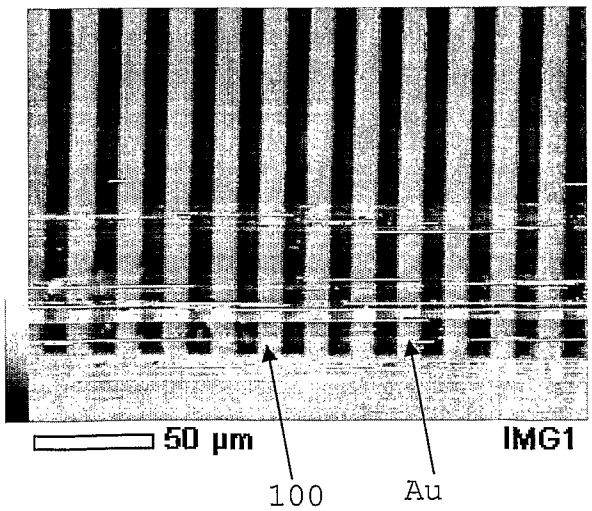


Fig. 17

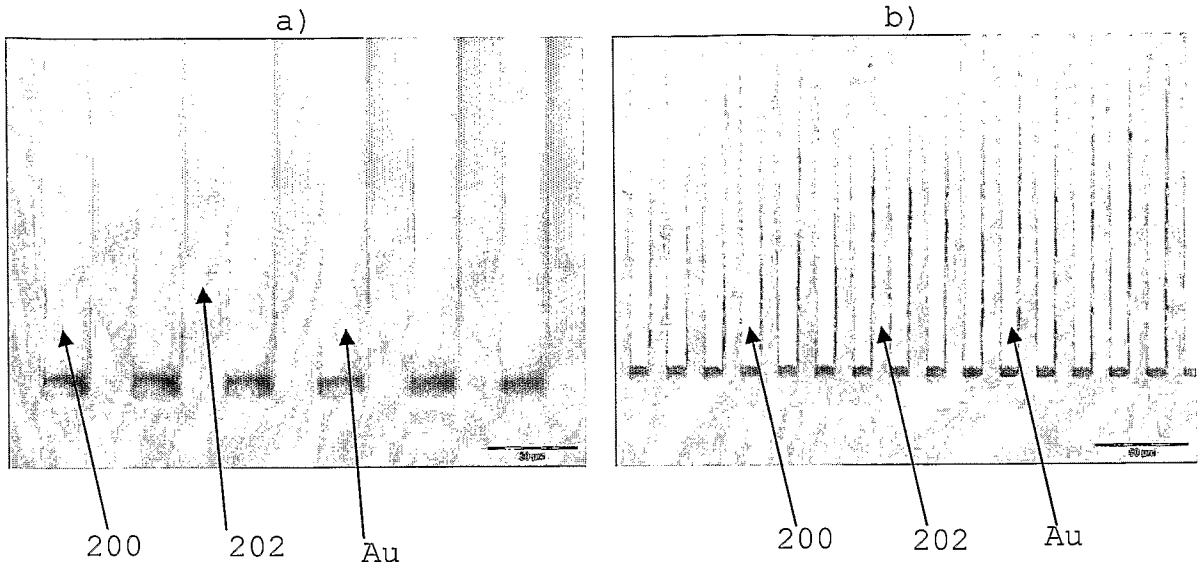


Fig. 18

INTERNATIONAL SEARCH REPORT

International application No.
PCT/SG2009/000373

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl.

H01L 51/40 (2006.01) ***G03F 7/00*** (2006.01)
B29C 59/02 (2006.01) ***H01L 21/46*** (2006.01)

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)

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

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
DWPI,EPODOC: H01L51/IC OR H01L21/46/IC OR G03F7/IC OR B29C59/IC „ +PRINT+ OR IMPRESS+ OR DEPRESS+ OR INDENT+ OR DENTAT+ OR STAMP+ OR PRESS+ OR M[O,OU]LD OR EMBOSS+, BASE? OR WAFER? OR SUBSTRATE? OR PLATE?, GOLD OR METAL OR CONDUCT+

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 2004/0121568 A1 (KIM et al) 24 June 2004. See fig 7	
A	US 2006/0188697 A1 (LEE) 24 August 2006 See fig 1A and para 58	
X	JP 2008-218459 A (TOYOTA MOTOR CORP) 18 September 2008. See para 10,14 of translation from http://www.ipdl.inpit.go.jp/homepg_e.ipdl	16-19,21,22, 25-28,30,31, 33-35
X,P	JP 2009-151062 A (ASTI CORP) 9 July 2009 See paras 9,15,16,24 of translation from http://www.ipdl.inpit.go.jp/homepg_e.ipdl	16,18,19,25,26,27,28,33,34
X	JP 2007-069604 A (TORAY IND INC) 22 March 2007 See fig 1, paras 33,51,52 of translation from http://www.ipdl.inpit.go.jp/homepg_e.ipdl	16-36

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* Special categories of cited documents:
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"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
18 January 2010	28 JAN 2010
Name and mailing address of the ISA/AU AUSTRALIAN PATENT OFFICE PO BOX 200, WODEN ACT 2606, AUSTRALIA E-mail address: pct@ipaustralia.gov.au Facsimile No. +61 2 6283 7999	Authorized officer **S. T. PRING** AUSTRALIAN PATENT OFFICE (ISO 9001 Quality Certified Service) Telephone No : +61 2 6283 2210

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/SG2009/000373

This Annex lists the known "A" publication level patent family members relating to the patent documents cited in the above-mentioned international search report. The Australian Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent Document Cited in Search Report		Patent Family Member					
US	2004121568	AU	2003298815	CN	1795570	EP	1573831
		KR	20050085858	US	2005170621	WO	2004061994
		WO	2007001409				
US	2006188697	CN	1838843	JP	2006216563	KR	20060089839
JP	2009151062		NONE				
JP	2008218459	CN	101578928	WO	2008105561		
JP	2007-069604		NONE				

Due to data integration issues this family listing may not include 10 digit Australian applications filed since May 2001.

END OF ANNEX