METHOD AND APPARATUS FOR MANUFACTURING A PATTERNED SUBSTRATE OR DEVICE

Field of Invention

The present invention relates to a method and an apparatus for manufacturing a patterned device or substrate for a device.

The present invention relates particularly, although by no means exclusively, to a method and apparatus for additive manufacturing of a patterned device or substrate for a device that utilises an electrochemical reaction to form a pattern on the surface of the substrate.

The present invention also relates particularly, although by no means exclusively, to a method and an apparatus for additive manufacturing of a conductive patterned device or substrate for an electronics device that utilises an electrochemical reaction to form a conductive pattern on the surface of the substrate.

Background

The current landscape of electronic device production is fraught with inefficiencies and limitations, primarily stemming from the predominant use of subtractive methods to produce circuits for the devices. Traditional approaches, characterized by multiple sequential steps and the use of distinct tools for patterning and deposition (or etching) of conductive surfaces, often lead to lengthy production timelines and high costs.

Additive manufacturing has the potential to revolutionize this landscape by streamlining processes, reducing steps, and minimizing capital requirements, thereby paving the way for more cost-effective manufacturing of electronic devices. However, the effective adoption of additive manufacturing in electronics faces formidable challenges. As electronics demand smaller feature sizes for enhanced performance, the inherent speed limitations of existing additive manufacturing technologies at high resolution pose a barrier to achieving scalable high-resolution production. Additionally, most additive technology simply cannot reach the feature sizes required for electronic devices.

Current solutions predominantly rely on photolithography for the fabrication of high-resolution devices, and screen printing or roll-to-roll methods for high throughput fabrication of lower resolution devices. However, these methods are beset by inefficiencies and limitations. Photolithography, while capable of high resolution, involves multiple sequential steps and substantial capital investment, resulting in slow and costly processes. Conversely, while screen printing offers higher throughput, its resolution and materials compatibility are limited, restricting its application and leading to elevated material costs and compromised conductivity of printed structures.

High resolution structures are desirable because they can provide more complex architectures which can enhance device performance. This can dramatically increase the total value of the manufacturing output.

In light of these challenges and limitations, there exists a need in electronic device manufacturing for a cost-effective and scalable manufacturing processes, particularly the development of a high throughput additive manufacturing technique that also has high-resolution capabilities.

Summary

Broadly, the present invention provides a method and an apparatus that utilises an electrochemical reaction for manufacturing a patterned device or substrate for a device. The geometry of the pattern is determined by a corresponding pattern embedded in the apparatus.

In an example, an apparatus for forming conductive elements on a substrate includes an insulator substrate, an electrode integrated with the insulator substrate, and an insulating pattern formed over the electrode, wherein the insulating pattern defines features that correspond to the conductive elements that are to be formed on the substrate.

In an example, the electrode has a two-dimensional footprint at an outwardly facing surface of the apparatus, and wherein multiple features are located within the two-dimensional footprint at the outwardly facing surface of the apparatus.

In an example, the electrode has a two-dimensional footprint at a front side of the apparatus, and wherein multiple features are located within the two-dimensional footprint at the front side of the apparatus.

In an example, the electrode has a front side portion with a two-dimensional area at a front side of the apparatus and a rear side portion with a two-dimensional area at a rear side of the apparatus, and wherein the two-dimensional area of the rear side portion of the electrode is greater than the two-dimensional area of the front side portion of the electrode.

In an example, the insulating pattern includes an insulating layer of insulating material, wherein the features are formed via photolithography.

In an example, the features have dimensions on the order of micrometers.

In an example, the features have dimensions on the order of nanometers.

In an example, the apparatus further includes electrodes, wherein the electrodes correspond to discrete conductive regions at an outwardly facing side of the apparatus.

In an example, the apparatus further includes multiple electrodes, wherein the electrodes correspond to discrete conductive regions at a front side of the apparatus.

In an example, the apparatus further includes multiple electrodes, wherein the electrodes correspond to discrete conductive regions at an outwardly facing surface of the apparatus, and wherein the electrodes are configured to be independently modulated with electrical potential and current.

In an example, the apparatus further includes multiple electrodes, wherein the electrodes correspond to discrete conductive regions at a front side of the apparatus, and wherein the electrodes are configured to be independently modulated with electrical potential and current.

In an example, the apparatus further includes a fluid channel within the insulator substrate, wherein an end of the fluid channel is at an outwardly facing side of the apparatus.

In an example, the apparatus further includes a fluid channel that passes through the insulator substrate from a front side of the apparatus to a rear side of the apparatus, wherein the fluid channel is configured to provide an ion source to the front side of the apparatus.

In an example, the apparatus further includes a fluid channel that passes through the insulator substrate, wherein the fluid channel is configured to provide an ion source to the outwardly facing side of the apparatus near the electrode.

In another example, an apparatus for forming conductive elements on a substrate includes an insulator substrate, electrodes integrated with the insulator substrate, wherein the electrodes correspond to discrete conductive regions of the apparatus, and an insulating pattern formed over the electrodes, wherein the insulating pattern defines features that correspond to the conductive elements that are to be formed on the substrate.

In an example, each of the electrodes has a front side portion with a two-dimensional area at a front side of the apparatus and a rear side portion with a two-dimensional area at a rear side of the apparatus, and wherein each of the electrodes is individually controllable.

Other aspects in accordance with the invention will become apparent from the following detailed description, taken in conjunction with the accompanying drawings, illustrated by way of example of the principles of the invention.

Brief Description of Drawings

Embodiments of the invention are hereinafter described by way of example only with reference to the accompanying drawings, wherein:

Figure 1(a) illustrates a pre-determined pattern on the conductive surface of a stamp electrode.

Figure 1(b) illustrates different ways of forming a conductive patterned substrate according to one form of the present invention.

Figure 2 illustrates various geometries of the stamp electrode according to one form of the present invention.

Figure 3 illustrates an exemplary apparatus according to one form of the present invention showing the location of the electric field.

Figure 4 illustrates a step-by-step rapid layer fabrication process according to one form of the present invention.

Figure 5 is a cross-sectional image of a patterned substrate formed using a contact technique using a continuous current according to one form of the present invention.

Figure 6 is a cross-sectional image of a patterned substrate formed using a contact-less technique using a continuous current according to one form of the present invention.

Fig. 7A is a side cutaway view of a stamp electrode that includes an insulator substrate, electrodes, and an insulating pattern.

Fig. 7B is a plan view of an example of the front side of a stamp electrode that shows various features that are formed by the insulating pattern at the front side of the stamp electrode.

Fig. 7C is a plan view of an example of the rear side of a stamp electrode that shows a portion of one or more electrodes of the stamp electrode.

Fig. 8A is a plan view of an example of the front side of a stamp electrode that shows multiple discrete conductive regions, with each discrete conductive region having various features that are formed by the insulating pattern at the front side of the stamp electrode.

Fig. 8B is a plan view of an example of the rear side of the stamp electrode 800 from Fig. 8A that shows a portion of the electrodes of the stamp electrode.

Fig. 9 is a side cutaway view of a stamp electrode that includes an insulator substrate, two electrodes, and an insulating pattern.

Fig. 10 is a side cutaway view of an example of a stamp electrode similar to the examples of electrode and electrode shown in Fig. 2.

Fig. 11A is a plan view of an example of the front side of a stamp electrode that shows multiple features formed by the insulating pattern, one end of each of four fluid channels, and an outline of a front side portion of an electrode.

Fig. 11B is a plan view of an example of the rear side of the stamp electrode from Fig. 11A that shows the opposite end of each of the four fluid channels as well as a rear side portion of the electrode that is visible at the rear side of the stamp electrode.

Fig. 12 is a side cutaway view of an example of a stamp electrode similar to the example described with reference to Figs. 10, 11A, and 11B.

Fig. 13 is a plan view of an example of the front side of a stamp electrode that shows one end of multiple fluid channels and an outline of the front side portion of two electrodes.

Fig. 14A is a side cutaway view of a stamp electrode that includes an insulator substrate, two electrodes, and an insulating pattern that defines features.

Fig. 14B is a plan view of an example of the front side of a stamp electrode that shows the front side portion of four electrodes and an outline of the rear side portion of the four electrodes.

Fig. 14C is a plan view of an example of the rear side of the stamp electrode from Fig. 14B that shows the rear side portion of the same four electrodes of the stamp electrode and an outline of the front side portion of the four electrodes.

Fig. 15A is a side cutaway view of a stamp electrode that includes an insulator substrate, two electrodes, and an insulating pattern that defines features.

Fig. 15B is a plan view of an example of the front side of a stamp electrode that shows features that are defined by an insulating pattern and an outline of the front side portion of four electrodes of the stamp electrode.

Fig. 15C is a plan view of an example of the rear side of the stamp electrode from Fig. 15B that shows the rear side portion of the same four electrodes of the stamp electrode and an outline of the corresponding front side portion of the four electrodes.

Detailed Description

It will be understood to persons skilled in the art of the invention that many modifications may be made without departing from the spirit and scope of the invention.

Broadly, the present invention provides a method and an apparatus that utilises an electrochemical reaction for manufacturing a patterned device or substrate for a device. The geometry of the pattern is determined by a corresponding pattern embedded in the apparatus.

The present invention also provides a method and an apparatus for additive manufacturing of a coated device or substrate for an electronic device using an electrochemical reaction to form a conductive coating having a predetermined pattern on the surface of the device or substrate.

The device or substrate may provide a conductive or non-conductive surface which can be patterned.

In this specification, any reference to a patterned substrate also refers to a patterned device which may consist of a patterned substrate *per se* or comprise a patterned substrate and one or more other components of the device. Correspondingly, any reference to the patterning of a substrate also refers to the patterning of a device consisting of the substrate.

In this specification, the term "device" encompasses optical devices, magnetic devices, electronic devices, data storage devices, optical metamaterials, sensors, chips, LASERS, LEDs, quantum sensing communication and computing devices.

In this specification, the term "electronic device" encompasses any device that conducts electricity. Non-limiting examples of electronic devices include printed circuit boards, solar cells, sensors, antenna, displays, batteries, and light emitting diodes.

In this specification, the term "pattern" encompasses 2D and 3D structures.

In particular, the present invention provides a method and an apparatus that utilises a spatially selective electrochemical reaction to modify the surface of a device or substrate to form a predetermined pattern.

In this specification, modification of the device or substrate surface can encompass any one of:

(i) modifying existing material on the device or substrate to altering the shape of the material to a predetermined pattern;
(ii) etching material from the surface of the device or substrate to form a predetermined pattern; and
(iii) depositing solid material on the device or substrate to form a coating having a predetermined pattern.

The present invention desirably provides a means to electrochemically modify the device or substrate surface by the application of a localised electric field to trigger the forming of a patterned coating on the device or substrate. Suitably, localisation of the electric field is facilitated by a stamp electrode which includes a patterned electrode surface with distinct regions that are insulating or conducting. This provides a predetermined pattern to which electrochemical reactions are limited to. Suitably, the formed pattern is re-usable for various applications.

The present invention was developed to ameliorate the problem of separate deposition and patterning steps to form a patterned layer on a device or substrate, particularly for semiconductor interconnects, which can be costly and time consuming. For example, photolithography requires an initial step of forming a photoresist layer that is etched in a subsequent step. In contrast, the present invention allows for the combination of the patterning and reaction steps to form the patterned device or substrate in which the layer for etching can be prior formed or be part of the device or substrate. The reaction step encompasses deposition of material on the device or substrate and etching and modification of the device or substrate or material on the device or substrate such as by oxidation or substitution.

The use of a spatially selective electrochemical reaction by the present provides a means of combining the reaction and patterning steps. The present invention is particularly applicable to additive manufacturing by providing a means of forming a 3D structure comprising multiple layers of deposited material on a device or substrate. Suitably, each layer of deposited material is formed with a predetermined pattern.

The present invention also improves localisation of material deposited on the device or substrate to improve resolution of the pattern on the device or substrate. In this specification, the lower bound limits of the term “high resolution” are <1,000 μm, suitably <200 μm, more suitably <100 μm, even more suitably <50 μm, yet even more suitably < 20μm, further yet even more suitably less than < 1μm. The upper bound limits of the term “high resolution” are >10 nm, suitably >100 nm, more suitably >1 μm, even more suitably >5 μm. The resolution may be independent of electrode area or reaction rate.

Another potential benefit of the invention is an ability to create, either by etching or depositing, a high aspect ratio structure in a single step. The present invention can also control reaction progression such as etching depth, height of deposited material, and morphology of formed structures by adjusting operating parameters such as voltage, pulse shape and ink formulation.

In a first aspect of the present invention, there is provided an apparatus for forming a high resolution patterned device or substrate for a device, the apparatus comprising:
a stamp electrode that is configured to form a pattern on a device or substrate, the electrode having an outwardly-facing surface on which is applied a mask having a predetermined pattern, wherein the stamp electrode is further configured to confine the electrochemical reaction to regions of the device or substrate less than 200 μm wide or deliver high current densities of greater than 10 kA/dm2 (or greater than 1 A/mm2) to the selected regions of the device or substrate during the electrochemical reaction;
an ion source to supply ions for forming a pattern on a device or substrate; and
a power supply to initiate movement of ions between the ion source and the device or substrate and an electrochemical reaction to form the pattern on the device or substrate, wherein the pattern is the same as or inverse to the predetermined pattern of the mask.

The stamp electrode may be configured to confine the electrochemical reaction to regions of the device or substrate less than 200 μm wide, suitably less than 100 μm wide, more suitably less than 50 μm wide, even more suitably 20 μm wide. This contributes to the production of a high resolution patterned device or substrate by enabling the manufacturer of intricate patterns within a confined space.

The stamp electrode may be configured to deliver high current densities of greater than 10 kA/dm2 (or greater than 1 A/mm2), suitably greater than 20 kA/dm2 (or greater than 2 A/mm2), more suitably greater than 50 kA/dm2 (or greater than 5 A/mm2), even more suitably greater than 80 kA/dm2 (or greater than 8 A/mm2). Current density is proportional to deposition rate and consequently production speed. Combined with the ability to form patterns within to regions of the device or substrate less than 200 μm wide, the present invention provides a means to achieve scalable high-resolution production.

The stamp electrode may be configured to confine the electrochemical reaction to regions of the device or substrate having a width to height aspect ratio of greater than 0.1, suitably greater than 0.2, more suitably greater than 0.5, even more suitably greater than 1.0.

The mask may be conductive or an insulator. The nature of the mask will depend on the nature of the outwardly-facing surface of the electrode. Specifically, the conductivity of the mask will be opposite to the conductivity of the outwardly-facing surface of the electrode. As a consequence, the mask will enable the formation of conducting and insulating regions on the outwardly-facing surface of the electrode.

The stamp electrode provides the active area for the electrochemical reaction by restricting the reaction to the exposed conductive region of either the stamp electrode or mask, and restricting it from the insulating region (i.e. to provide a spatially selective reaction). This allows the deposition (or etching, anodising etc) and patterning steps to be combined.

The stamp electrode may comprise a conductive, semi-conductive or insulating base over which the conductive and insulating regions are located.

The conductive region may be part of the base or an additional layer, such as an electrode, located on the base.

The insulating region may be formed by a patterned insulating mask applied on a conductive surface of the electrode. The insulating mask pattern enables the formation of electrochemically transformed regions of the device or substrate surface having an inverse pattern to the insulating mask pattern during the electrochemical reaction.

Suitably, the stamp electrode is an anode and the device or substrate is a cathode when a reductive reaction is to be performed on the device or substrate, such as the deposition of metal. In another embodiment, the stamp electrode is a cathode and the device or substrate is an anode if electropolymerization or any other oxidative reaction is performed on the device or substrate.

The outwardly-facing surface may be substantially flat. In some embodiments, the outwardly-facing surface contains non-planar features. Suitably, the non-planar features are raised or recessed regions.

The outwardly-facing surface may comprise multiple discrete conductive regions, wherein the electrical potential and current of each region can be independently modulated. By providing multiple independent conductive regions, the electrochemical reaction at each region can be adjusted as required. For example, the current delivered to each region may be adjusted to account for the voltage drop and ensure that the reaction conditions are uniform across the discrete regions. The inverse is also true, in which multiple conducting regions allow for non-uniform deposition, giving regions of different film thickness during a single patterning step. This is not possible for photolithography and screen printing.

The base may be made from an inert material. Suitably, the material is a noble metal, conductive polymer, a semiconductor or carbon allotrope. Non-limiting examples of suitable materials include metals such as nickel, copper, platinum, gold, silver, steel alloys, conductive polymers such as Poly(3,4-ethylenedioxythiophene) (PEDOT), semiconductors (doped or undoped) such as silicon, gallium arsenide, indium phosphide, germanium, conductive oxides such as indium tin oxide (ITO), and carbon allotropes.

The stamp electrode may include a conductor located between the base and an insulating mask. Suitably, the conductor comprises an inert material. More suitably, the inert material may comprise a noble metal, conductive polymer, a semiconductor or an allotrope of carbon. Even more suitably, the inert material is different to the material of the conductive base. Non-limiting suitable examples of the inert material for the conductor are the same as for the conductive base.

Having a base and/or the intermediate conductor that is inert to electrochemical conditions improves durability of the stamp electrode to multiple deposition cycles.

The outwardly-facing surface incorporating the mask may form a topography that aligns and accommodates the device or substrate surface or with the product of a previous electrochemical reaction on the device or substrate surface.

The Applicant realised that a stamp electrode with diverse surface topography is advantageously suited to multi-layer electrochemical modification. In this respect, the topography of the outwardly-facing surface can advantageously be manipulated to accommodate a non-uniform and/or non-flat device or substrate topography, or with the product on a previously electrochemically modified device or substrate.

The pattern formed on the device or substrate is defined by the arrangement of conductive and non-conductive regions on the stamp electrode relative to each other.

The pattern may be conductive. Suitably, the pattern is formed from conductive material.

The mask is one feature of the apparatus that determines the pattern formed on the device or substrate.

The mask forms a spatially selective patterned surface on the outwardly-facing surface of the stamp electrode which determines the electrochemically transformed regions of the device or substrate surface.

During electrochemical reaction, depending on the conductive properties of the mask and outwardly-facing surface of the stamp electrode, the electrochemical reaction can either occur on the device or substrate position over the mask or in the exposed regions around the mask. For example, regions on the device or substrate positioned over the electrode insulating mask are isolated from the electrochemical reaction and remain substantially unmodified. Exposed device or substrate regions positioned over the conductive surface of the electrode are modified by the electrochemical reaction. Conversely, regions on the device or substrate positioned over the electrode conductive mask are modified by the electrochemical reaction while exposed device or substrate regions positioned over the insulating surface of the electrode are shielded from the electrochemical reaction.

The mask may be applied to, and protrude from, the surface of the stamp electrode. In some embodiments, the mask is recessed into the electrode surface.

The material of the mask is not particularly limited. The insulating material may be mechanically rigid (i.e. exhibit a high Young's modulus), or may be mechanically flexible

and/or elastic (i.e. exhibit a low Young's modulus). Suitable materials for forming an insulating mask may include inorganic dielectrics such as silicon dioxide, aluminium oxide, tantalum oxide, silicon nitride, silicon carbide, and include polymers such as SU-8, polydimethylsiloxane (PDMS), polymethyl methacrylate (PMMA), epoxies, Polytetrafluoroethylene (PTFE), polythene (PE), polyether ether ketone (PEEK), rubbers, polyimides and polyolefins. Suitable materials for forming a conductive mask may include materials such as nickel, copper, tin, chromium, aluminium, molybdenum, tungsten , indium, platinum, gold, silver, steel alloys, conductive polymers such as Poly(3,4-ethylenedioxythiophene) (PEDOT), semiconductors (doped or undoped) such as silicon, gallium arsenide, indium phosphide, germanium, conductive oxides such as indium tin oxide (ITO), and carbon allotropes.

Advantageously, when the mask is flexible and/or elastic, the mask should preferably deform on contact with the device or substrate, and conform at least partially to the surface of the device or substrate.

A flexible and/or elastic mask that can conform to the topology of the device or substrate may provide distinct advantages, including:

(i) alignment of the stamp electrode and device or substrate;

(ii) mechanical leveling of the material on the device or substrate;

(iii) defining the electric field by confining the reaction media to conductive regions of the stamp electrode; and

(iv) creating a sharp edge definition in electric field where the ions are confined to provide sharp and high resolution patterning and reduce unwanted reactions from taking place such as excessive deposition and/or target surface damage or contamination.

The mask may comprise a rigid polymer. A rigid polymer for the mask may enable the mask to be used to set the interelectrode gap in an embodiment where the polymer projects from the outwardly-facing surface of the electrode, and the mask contacts the device or substrate during the electrochemical reaction.

The mask may comprise a soft polymer that is conformable to the surface of the device or substrate.

The soft polymer may have a Young's Modulus of less than 1,000 MPa, suitably less than 100 MPa, more suitably less than 10 MPa. This enables the soft polymer to reach the required strain of less than 5%, suitably less than 3%, more suitably less than 1% to conform to the target device or substrate surface, even more suitably ranging from 5-0.01%.

The platform may be movable to adjust the position of the device or substrate relative to the stamp electrode.

The apparatus may be configured to adjust the position of the stamp electrode relative to the device or substrate. Suitably, the stamp electrode is mounted to a movable arm of the apparatus.

The apparatus may include a platform for supporting a device or substrate.

The platform may be configured to receive an ion transfer medium for facilitating movement of ions between the device or substrate and an ion source to form the coating. Suitably, the platform forms a receptacle to contain the ion transfer medium, and allow a device or substrate to be submerged in the medium. Alternatively, the ion transfer medium can be applied onto the device or substrate directly. Suitably, the ion transfer medium is applied onto the device or substrate such that it is confined to the top surface of the device or substrate. More suitably, the at least one thin layer of the ion transfer medium is applied onto the device or substrate without contacting the bottom and side edges of the device or substrate.

Non-limiting examples of the ion transfer medium include ion-containing inks, one or more organic, ionic and aqueous solvents such as water, aqueous solutions, polar or apolar hydrocarbon solutions, deep eutectic solvents, inorganic hot melts, ionic liquids, solid conductors of ions such as superionic polymers and oxides, and supercritical fluids such as CO_2. The ion transfer medium may comprise a selective membrane that can be used with a solvent.

The ion source may be solid material deposited on the stamp electrode, be part of the stamp electrode or in the form of an ink. A separate ion transfer medium may not be necessary if an ink is used, which is a source of ions and a medium for transporting the ions.

The ink may comprise a mixture of at least two substances. Non-limiting examples of substances for the ink include water, sulphuric acid, hydrochloric acid, copper sulphate, potassium chloride copper nitrate, copper chloride, copper cyanide, potassium hydroxide, potassium carbonate, nickel sulphate, nickel chloride, boric acid, and nickel sulfamate. The ink may also include one or more of organic, ionic and aqueous solvents such as aqueous solutions, polar or apolar hydrocarbon solutions, deep eutectic solvents, inorganic hot melts, ionic liquids, solid conductors of ions such as superionic polymers and oxides, and supercritical fluids such as CO_2.

The ink may include one or more additives to modify the liquid properties of the ink. Suitable additives include a surfactant to modify wetting properties, a humectant to modify viscosity, and a cosolvent to modify solubility of ink ingredients.

The stamp electrode may be configured to deliver, for example by injection, an ink to the outwardly-facing surface of the stamp electrode.

Suitable stamp electrode configurations can include one of more of the following features:

(i) channels for delivering ink to the surface;

(ii) a microfluidic circuit to deliver the ink to the surface;

(iii) a porous structure; and

(iv) a membrane.

The same stamp electrode configuration may also deliver the ink to a device or substrate.

The apparatus is configured to be used with a range of devices or substrates.

The device or substrate may comprise a conductive material. It may itself act as an electrode, optionally as a counter electrode or a working electrode. It may, for example, comprise indium tin oxide (ITO), silicon, aluminium, carbon, steel, copper, gold, nickel, platinum, indium, or a combination thereof. A skilled person will understand that the size and shape of the device or substrate may be selected for the pattern intended to be fabricated thereupon. In certain embodiments, the device or substrate may provide a substantially flat surface on which to form the pattern. The device or substrate may be rigid or flexible.

The device or substrate may be capable of retaining an ion source or an ion transfer medium on its surface. Suitably, the device or substrate is shaped to retain an ion transfer medium over its surface.

The device or substrate may be surface treated to modify the wettability of liquid ion sources deposited on the device or substrate surface.

The power supply is configured to generate an electric field. Suitably, the power supply generates a potential difference between the stamp electrode and the device or substrate to enable flow of ions from the ion source to the device or substrate and trigger the electrochemical reaction. More suitably, the potential difference facilitates electron transfer which triggers the electrochemical reaction. The voltage delivered by the power supply may depend on many factors including the reaction type, the solvent, the counter ions, temperature, pH, pressure, and interelectrode gap.

Broadly, the voltage for copper deposition ranges from 0.2-15V, suitably ranges from 0.4V and 2V. A skilled person would appreciate that other reactions may require a negative voltage.

The power supply may deliver a time varying current, including but not limited to an AC signal, a sequence of current values, and/or ultra-short pulses of current. Without being bound by theory, it is believed that ultra-short pulse current, suitably having a pulse length ranging from nanoseconds to milliseconds, can assist in localising the electric field by only locally polarising/unpolarising the double layer. The distance that the transient electric field travels from the electrode on the stamp electrode is proportional to pulse time, so shorter pulses translate to smaller fields, i.e. more localisation. Ultra-short pulse current can also assist with improving reaction rate, uniformity and control over the reaction more generally. An AC signal offset to the plating voltage can increase the quality of a deposited film by disrupting the Debye Layer as well as modifying the z-uniformity.

The ultra-short pulse current may be an alternating current. Suitably, the alternating current signal is offset to the voltage delivered to the stamp electrode.

The ultra-short pulse current may have a pulse length in the milli-second range. Suitably, the ultra-short pulse current has a pulse length ranging from nanoseconds to microseconds to milliseconds. The duty cycle of the pulse current may take a broad range of values, from less than 0.1% to approaching unity.

In a second aspect of the present invention, there is provided a method of forming a high resolution patterned device or substrate for a device using an apparatus comprising a stamp electrode having an outwardly-facing surface on which is applied a mask having a predetermined pattern; an ion source to supply ions for forming a pattern on a device or substrate; and a power supply to initiate movement of ions between the ion source and the device or substrate and an electrochemical reaction to form the pattern on the device or substrate, the method including:
providing a device or substrate;
positioning the stamp electrode relative to the device or substrate to enable movement of ions between the ion source and the device or substrate; and
delivering high current densities of greater than 10 kA/dm2 (or greater than 1 A/mm2) to the selected regions of the device or substrate during the electrochemical reaction to generate an electric field and/or confining the electrochemical reaction to regions of the device or substrate less than 200 μm wide to form the pattern on the device or substrate, wherein the pattern is the same or inverse to the predetermined pattern of the mask.

The method may be performed using the previously described apparatus.

A feature of the method is a spatially and temporally defined electrochemical reaction that is initiated by an electric field. This reaction enables the formation of the predetermined pattern on the device or substrate as a layer (e.g. as an imprint) unlike vector or array based additive manufacturing techniques which form the pattern line-by-line or one pixel at a time.

The potential difference across the stamp electrode and device or substrate provides a motive force to initiate the electrochemical reaction. The potential difference generates an electric field to drive the electrochemical reaction. The reaction may add material, subtract material, or modify material on the device or substrate to form the predetermined pattern.

The electrochemical reaction may be one or more of electrochemical deposition, etching, and/or in situ transformation of solid material on the device or substrate.

Deposition refers to the addition of solid material onto the device or substrate surface, for example by electrochemical reduction of a solid metal, or electropolymerisation of a polymer, onto the device or substrate surface. Etching refers to removal of solid material from the device or substrate surface, for example by electrochemical oxidation and partial dissolution of the device or substrate surface or pre-existing solid material on the device or substrate. In situ transformation refers to any electrochemical reaction that alters the device or substrate surface, suitably through reduction or oxidation, without substantially adding or removing solid material from the device or substrate. Suitable techniques that effect in situ transformation include anodisation, surface functionalisation and photoresist development.

The method may include providing a device or substrate that is capable of retaining an ion source or an ion transfer medium on its surface.

The method may include surface treating the device or substrate to modify the wettability of liquid ion sources deposited on the device or substrate surface.

The method may include providing a mask comprising a soft polymer, that may be conformable to the surface of the device or substrate. Suitably, the soft polymer may conform to the surface of the device or substrate by pressing the soft polymer onto the surface of the device or substrate using a pressure, suitably ranging from 0.01 MPa to 10 MPa.

The method may include applying the mask on the outwardly-facing surface of the stamp electrode. During the electrochemical reaction, regions on the device or substrate positioned over the insulating regions of either the outwardly-facing surface of the stamp electrode or mask do not participate in the electrochemical reaction. Device or substrate regions positioned over the surrounding exposed conductive regions undergo reaction.

The method may include applying or forming the mask directly onto the outwardly-facing surface of the stamp electrode.

In embodiment in which the stamp electrode comprises a conductive base and an outwardly facing conductor, the method includes applying or forming the insulating mask onto the conductor.

The method may involve altering the topography of the surface of the stamp electrode. The step of altering the topography of the surface of the stamp electrode may be to provide a substantially planar or non-planar outwardly facing surface of the stamp electrode for initiating the electrochemical reaction.

The method may include altering the topography of the outwardly-facing surface of the stamp electrode to form a substantially planar outwardly facing surface of the stamp electrode. In this embodiment, the outwardly-facing surface may have an inverse pattern to the mask such that application of the mask to the recessed pattern of the surface provides a substantially planar outwardly facing surface of the stamp electrode.

The method may include altering the topography of the outwardly-facing surface of the stamp electrode to form a substantially non-planar outwardly facing surface of the stamp electrode. This may be done to accommodate interaction with a non-flat device or substrate or with a device or substrate that has been previously electrochemically modified. This may be achieved by any one or more of:

(i) providing a stamp electrode having a non-planar outwardly-facing surface;
(ii) using a mask with varying thickness having an opposing conductivity to the outwardly-facing surface of the stamp electrode; and
(iii) selectively applying the mask to the surface of the stamp electrode to provide a surface morphology that mirrors the surface morphology of the device or substrate.

In an embodiment wherein the outwardly-facing surface of the stamp electrode comprises multiple discrete conductive regions, the method may include applying a current to each independent conductive region. Suitably, the method includes modulating the current applied to each independent conductive region to provide uniform electrochemical conditions across the device or substrate surface. More suitably, the step of modulating the current includes takes into account voltage drop across each region.

The method may include providing a stamp electrode formed from an inert material. Suitably, the method may include providing a stamp electrode having a conductive base formed from an inert material.

The method may include providing a stamp electrode including a conductor located between the base and insulating mask. Suitably, the method includes providing a stamp electrode including a conductor comprises an inert material located between the base and insulating mask. More suitably, the method includes providing a stamp electrode including a conductor made from an inert material that is different to the material of the base.

The method may include providing an ion transfer medium. Suitably, the method may include delivering the ion transfer medium to the platform.

The positioning step may include contacting the device or substrate with an ion source or an ion transfer medium. The ion source or ion transfer medium forms a bridge between the electrode stamp and the device or substrate to enable movement of ions between the two components.

The method may include positioning a device or substrate on a platform. The platform supports the device or substrate during the electrochemical reaction.

The positioning step may include moving the stamp electrode so that it is either in contact with, or separated by an interelectrode gap from, the device or substrate. Suitably, the method positioning step may include moving the platform to adjust the position of the device or substrate relative to the stamp electrode.

The method may include contacting the mask with the device or substrate. When the insulating material contacts the device or substrate, the interelectrode gap (i.e. the gap between the stamp electrode and the device or substrate) may be defined by the thickness of the mask.

The method may involve maintaining an interelectrode gap between the stamp electrode and device or substrate. Suitably, the gap is a maximum of 1,000 μm. More suitably, the gap is less than 5 μm.

The minimisation of the interelectrode gap is based on the Applicant's understanding that a smaller gap produces an inversely larger electric field intensity, and a lower media impedance, which in turn produces a higher current density (and thus reaction rate) for a given potential voltage. Compared to traditional large area plating, this can significantly improve deposition rates for the same material quality.

The method may include applying the ion transfer medium on the surface of the device or substrate. Suitably, the method step includes submerging the device or substrate in the ion transfer medium.

The method may include positioning the device or substrate to retain the ion transfer medium over its surface.

The method may include providing an ink as the ion source.

The method may include delivering the ion source to the outwardly-facing surface of the stamp electrode. Suitably, the method includes delivering an ink to the outwardly-facing surface of the stamp electrode.

The method may include selectively wetting regions of the stamp electrode to control location of the ion transfer medium on the exposed surface of the stamp electrode.

In an embodiment wherein the ion transfer medium is an ink, the method may include loading the ink onto either the stamp electrode or target device or substrate surface. Suitably, the method includes delivering the ink onto the device or substrate via one or more of the ways:

(i) injection;
(ii) channels in the stamp electrode;
(iii) microfluidic circuit;
(iv) a porous structure; and
(v) membrane.

The method may include selectively wetting regions of the outwardly-facing surface to control location of the ink on the stamp electrode.

The method may include determining the magnitude of the electric field by taking into account one or more of the size and material of the stamp electrode used, size and material of device or substrate, ion transfer medium conductivity, potential difference applied, and the interelectrode gap between the stamp electrode and the device or substrate.

The method may include measuring the current applied to generate the potential difference between the device or substrate and the stamp electrode as a function of time. Measuring the current allows for tracking of the deposition rate to control deposition thickness. It also could be used to optimise deposition parameters (such as inter-electrode gap, applied voltage, temperature, ink agitation etc.) on a substrate-by-substrate or device-by-device basis. Suitably, the method includes measuring the current applied to generate the potential difference between the device or substrate and the stamp electrode at a plurality of intervals. The intervals are less than the pulse time. Suitable examples of the time intervals are 1 μs to 10 seconds apart, from 100 μs to 1 second apart, 1 ms to 1 second apart, or 0.1 second to 1 second apart. More suitably, the time points are 1 μs, 2, μs, 5, μs, 10, μs, 20 μs, 50 μs, 100 μs, 200 μs, 500 μs, 1 ms, 2 ms, 5 ms, 10 ms, 20 ms, 50 ms, 0.1 sec, 0.2 sec, 0.5 sec, 1 sec, 2 sec, 5 sec, or 10 seconds apart.

The method may include monitoring the current supplied to generate the potential difference.

The method may include closed loop control of the voltage and/or current.

The method may include increasing the potential difference between the device or substrate and the stamp electrode, and/or decreasing the distance between the stamp electrode and the device or substrate or material applied to the device or substrate, when the current is below the predetermined value.

The method may include augmenting the electric field with a secondary field including one or more of the following fields:
a) laser fields (pulsed and continuous);
b) magnetic fields (pulsed and continuous);
c) ultrasonic fields (pulsed and continuous);
d) fluid fields; and

e) secondary electric fields (potentially through a dielectric).

The method may include repeating the step of applying a potential difference across the stamp electrode and device or substrate after an initial conductive pattern is formed on the device or substrate. This enables the formation of a layered 3D conductive structure. The subsequent conductive patterns, suitably in the form of layers of conductive material, may partially or completely overlap the previous conductive patterns.

The method may include connecting the power supply such that the stamp electrode is an anode and the device or substrate is a cathode.

In a third aspect of the present invention, there is provided a method of forming a patterned device or substrate for a device using an apparatus comprising a stamp electrode having an outwardly-facing surface on which is applied a mask having a predetermined pattern, wherein the insulating mask comprises a polymer that is selected to contact and conform to the surface of the device or substrate; an ion source to supply ions for forming the pattern on the device or substrate; and a power supply to generate a potential difference between the stamp electrode and the device or substrate, the method including:
providing a device or substrate;
contacting the mask with the device or substrate to conform the mask with the surface of the device or substrate; and
applying a potential difference across the stamp electrode and the device or substrate to generate an electric field to initiate an electrochemical reaction to form the pattern on the device or substrate, wherein the pattern is the same as or inverse to the predetermined pattern of the mask.

The insulating mask may comprise a soft polymer. The use of a soft polymer is particularly beneficial to provide patterned devices or substrates having higher resolutions.

In a fourth aspect of the present invention, there is provided a method of forming a patterned device or substrate for a device using an apparatus comprising a stamp electrode having an outwardly-facing surface on which is applied a mask having a predetermined pattern; an ion source to supply ions for forming the pattern on the device or substrate; and a power supply

to generate a potential difference between the stamp electrode and the device or substrate, the method including:
providing a device or substrate;
positioning the stamp electrode relative to the device or substrate to enable movement of ions between the ion source and the device or substrate; and
applying a potential difference across the stamp electrode and the device or substrate to generate an electric field and an ultra-short pulse current to initiate an electrochemical reaction to form the pattern on the device or substrate, wherein the pattern is the same as or inverse to the predetermined pattern of the mask.

One aspect of the present invention provides a method of forming a conductive patterned substrate for an electronic device.

The method involves localised electrochemical surface modification of a substrate to form the conductive pattern. The method is performed using an apparatus including a stamp electrode having an outwardly-facing conductive surface including an insulating mask having a predetermined pattern.

Electrochemical surface modification

In accordance with the present invention, modification of the substrate is achieved by subjecting the substrate surface to an electrochemical reaction. The electrochemical reaction can involve electrochemical deposition, etching, and/or in-situ transformation. Figure 1(b) provides exemplary illustrations of these reactions.

The electrochemical reaction can be initiated by generating a potential difference across a precursor-containing solution. This enables flow of ions from the ion source to the substrate and trigger the electrochemical reaction. For copper deposition, this would consist of a precursor solution containing dissolved copper ions in which the copper ions are driven by the electric field towards the substrate surface, and being reduced to solid copper on the surface.

Reaction 1 in Figure 1(b) illustrates an additive reaction involving the deposition of conductive solid material 10 onto the surface of substrate 12. The deposition of material can

occur by electrochemical reduction of metallic cations or precipitation of solid metal onto the substrate surface.

Reaction 2 in Figure 1(b) illustrates a substrative reaction in the form of etching. This reaction involves removal of solid material 10 from the surface of substrate 12 to leave a patterned solid material 13. The etching process can occur by electrochemical oxidation and partial dissolution of the substrate surface.

Reaction 3 in Figure 1(b) illustrates an in-situ transformation reaction which involves altering the chemical and/or physical properties of the solid material 10 deposited on the substrate. The transformation can occur via various reactions including reduction, oxidation, conjugation and functionalisation without substantially adding or removing material from the substrate. In Figure 1(b), the central portion 14 of solid material 10 is converted into a different material.

Patterned stamp electrode

The reaction is initiated by an electric field which enables the flow of ions to and/or from the substrate. The electric field is generated by an apparatus comprising a stamp electrode, a platform to support a substrate, an ion source to supply ions for forming the conductive pattern, and a power supply to generate an electric field by forming a potential difference between the stamp electrode and the substrate.

A key component of the apparatus is the stamp electrode which comprises a conductive base and an outwardly-facing insulating mask having a predetermined pattern. The stamp electrode including the insulating mask enables replication of an inverse pattern onto a substrate.

In one example, the stamp electrode is formed from a piece of metal to provide a conductive body onto which an insulating mask is applied.

The stamp electrode may have an outwardly-facing surface that is substantially flat. Alternatively, the topography of the electrode surface can be manipulated to accommodate interaction with a non-planar substrate, or with substrate that has been previously

electrochemically modified to form an initial conductive pattern on the substrate that is to be further modified, for example by additive or subtractive process.

Selection of the material used to form the insulating mask may depend on the method of patterning the substrate.

In a first example, the pattern is formed using a contact-less technique in which an interelectrode gap is maintained between the stamp electrode and the substrate for the duration of the patterning step. In this example, the insulating mask may be formed from a a wide range of materials that encompasses mechanically rigid (i.e. exhibit a high Young's modulus), and mechanically flexible and/or elastic (i.e. exhibit a low Young's modulus) materials.

In a second example, the pattern is formed using a contact technique in which the stamp electrode contacts the substrate for the duration of the patterning step. In this example, the stamp electrode may include an insulating mask that projects from an outwardly-facing surface of the electrode to create an enclosed region for reaction, and accurately set the interelectrode gap.

To improve the reaction process within these enclosed regions, a soft polymer, typically having a Young's Modulus of less than 30 MPa, may be used for the insulating mask. The soft polymer enables the insulating mask to deform on contact with the substrate, and conforms to the surface of the substrate to enhance the seal between the stamp electrode and substrate. The improved seal is particularly important to form higher resolution patterned substrates.

In use, regions on the substrate overlapping the insulating mask are isolated from electrochemical reaction and remain substantially unmodified. Substrate regions overlapping the conductive electrode material participate in the electrochemical process. Figure 1(a) illustrates an example of a pattern formed on the outwardly-facing conductive surface of the stamp electrode by the insulating mask 16. Reaction occurs on the exposed unhatched area 18 of the surface while the covered hatched area of the electrode surface is protected from reaction.

Figure 2 provides exemplary illustrations of suitable stamp electrodes.

Electrode 1 of Figure 2 comprises a metal base 20 and an outwardly-facing insulating coating 22 having a predetermined pattern that directly contacts the base.

Electrode 2 of Figure 2 is a variation of Electrode 1 further including an inert conductor 24 sandwiched between the metal base 20 and insulating mask 16. In this electrode, the insulating mask 16 directly contacts the inert conductor 24.

Electrode 3 of Figure 2 is a variation of Electrode 1 wherein the surface of metal base 20 is contoured and the recesses on the contoured surface are occupied by an insulating mask 16 to form a substantially flat outwardly-facing conductive surface.

Electrode 4 of Figure 2 is a variation of Electrode 3 further including an inert conductive 24 sandwiched between the metal base 20 and insulating mask 16. The inert conductor 24 conforms to the contours of the metal base 20 with the insulating mask 16 filling the recesses formed on the inert conductor 24 to form a substantially flat outwardly-facing conductive surface.

Electrode 5 of Figure 2 is a variation of Electrode 2 wherein the inert conductor 24 and the insulating mask 16 are co-planar and form a substantially flat outwardly-facing stamp electrode surface.

Electrode 6 of Figure 2 wherein the conductive metal base is in the form of a pair of structures 28 having an I-shape cross-section embedded within an insulator body 30. The exposed regions of the conductive metal base are overlaid with an inert conductor 24 to form a non-planar pattern.

Electrode 7 of Figure 2 is a variation of Electrode 1 wherein the insulating mask comprises a soft polymer 32 that is configured to contact and conform to the surface morphology of a substrate.

Electrode 8 of Figure 2 is a variation of Electrode 7 wherein the inert metal conductor 24 is sandwiched between the metal base 20 and the soft polymer 32.

Electrode 9 of Figure 2 is a pre-plated variation of Electrode 8 including deposit 34.

Electrode 10 of Figure 2 is a variation of Electrode 6 wherein a number of channels 36 extend through the insulator body 30 for injecting ink onto the substrate 12.

Electrode 11 of Figure 2 comprises a conductive metal base 20 covered with the inert conductor 24 and possessing a porous structure that allows ink and ions to flow through the metal base. The metal base is embedded within an insulator body 30 having an inwardly-facing surface that is shaped into a receptacle to contain a volume of ink 38.

Apparatus

The stamp electrode is one component of an apparatus according to the present invention that enables the production of the conductive patterned substrate. Another component of the apparatus is the substrate on which the conductive pattern is formed.

In one embodiment, the substrate is formed from a conductive material which may include one or more of indium tin oxide (ITO), silicon, aluminium, steel, gold, or a combination thereof. This substrate possesses a rigid planar surface on which the conductive pattern is imprinted.

The stamp electrode and substrate form a cathode-anode pair in which the stamp electrode is the anode and the substrate is the cathode.

The apparatus further includes an ion source to provide ions for forming the conductive pattern. The ion source may be solid material deposited on the stamp electrode or be part of the stamp electrode.

Alternatively, the ion source is an ion-containing fluid, preferably an ion-containing liquid. For example, the Electrode 10 and 11 illustrations in Figure 2 show the ion source in the form of ink 38. One benefit of using ink as the ion source is that a separate ion transfer medium is not required for the electrochemical reaction.

The ink can include water, sulphuric acid, hydrochloric acid, copper sulphate, potassium chloride copper nitrate, copper cyanide, potassium hydroxide, potassium carbonate, nickel sulphate, nickel chloride, boric acid, and nickel sulfamate.

Another component of the apparatus is a power supply that generates a potential difference between the stamp electrode and the substrate to enable flow of ions from the ion source to the substrate. The potential difference also facilitates electron transfer which triggers the electrochemical reaction. Figure 3 illustrates a stamp electrode in operation showing electric field lines radiating from the inert conductor 24.

The apparatus also includes a platform for supporting the substrate which can be in the form of a container that can contain a liquid ion source and/or ion transfer medium.

Method

The present invention provides two main methods of forming the conductive patterned substrate.

Contact-less technique

The first method is a contact-less technique in which an interelectrode gap is maintained between the stamp electrode and the substrate for the duration of the patterning step. The stamp electrode avoids contacting the substrate for the duration of the patterning step.

Figure 4 illustrates a rapid layer fabrication process that is performed using the contact-less technique using an apparatus comprising Electrode 5 of Figure 2.

Step 1 involves loading ink 38 onto the outwardly-facing surface of the stamp electrode which comprises conductor 24 and the insulating mask 16 in a co-planar arrangement. Regions of the surface may be selectively wetted to control the location of the ink on the stamp electrode.

Depending on the patterning mode, the next step of the process can either be step 2A or step 2B. Step 2A involves a deposition patterning step and Step 2B involves an etching patterning step.

Deposit patterning

In Step 2A, the stamp electrode is positioned over the substrate 12 and lowered until the ink 38 forms a fluid bridge between the stamp electrode and the substrate 12. In some embodiments, the apparatus is configured to position the stamp electrode to form a predetermined gap between the stamp electrode and the substrate 12. The Applicant deliberately utilises a very small interelectrode gap to significantly improve the deposition rate.

In Step 3A, a potential difference is applied between the stamp electrode and the substrate to deposit solid material 10 onto regions of the substrate overlapping the inert conductor 24 to form a pattern that is inverse to the pattern of the insulating mask.

In Step 4A, the stamp electrode is removed and the patterned substrate comprising deposited material 10 is washed to obtain the final product.

Etch patterning

In Step 2B, the stamp electrode is positioned over a substrate 12 having a pre-existing layer of conductive material 10. The stamp electrode is lowered until the ink 38 forms a bridge between the stamp electrode and the pre-existing layer of conductive material 10.

In Step 3B, a potential difference is applied between the stamp electrode and the substrate. This causes dissolution of regions of the pre-existing layer of conductive material 10 overlapping the inert conductor 24 to etch a pattern into the conductive material and form patterned conductive solid material 13.

In Step 4B, the stamp electrode is removed and the substrate 12 is washed to obtain the final product.

Contact technique

The second method is a contact technique in which the insulating mask contacts the substrate for the duration of the patterning step.

The insulating mask projects from the outwardly-facing surface of the electrode and encloses conductive regions of the outwardly-facing surface for the electrochemical reaction. The mask can be made from rigid or soft material. One benefit of using a rigid material for the mask is that the mask can be used to accurately set the interelectrode gap.

Alternatively, if a higher resolution patterned substrate is desired, the mask can be made from a soft material, typically having a Young's Modulus of less than 30 MPa. The flexibility of the mask enables the insulating mask to better conform to the surface of the substrate and form a better seal around the conductive regions of the outwardly-facing surface.

In operation, the stamp electrode is positioned over the substrate and lowered until the insulating mask contacts the substrate. A potential difference is then applied between the stamp electrode and the substrate to deposit solid material such as copper, suitably derived from ink or ion transfer medium. The ink can containing any one or more of water, sulphuric acid, hydrochloric acid, copper sulphate, potassium chloride copper nitrate, copper cyanide, potassium hydroxide, potassium carbonate, nickel sulphate, nickel chloride, boric acid, and nickel sulfamate onto exposed regions of the electrode around the insulating mask.

Subsequently, the stamp electrode is removed and the patterned substrate is washed to obtain the final product.

The contact technique provides two main advantages over the contact-less technique.

The first advantage is the ability to mechanically level the deposited material on the substrate prior to the electrochemical reaction. This can improve the structural integrity of the final product by compacting the deposited material.

The second advantage is improved resolution of the final product. This is because contact between the insulating mask and the substrate or pre-existing conductive layer on the substrate confines the reaction media to regions under the conductive regions of the stamp electrode and provides a sharp edge definition to the electric field where the reaction media ends. This in turn reduces unwanted reactions such as over deposition and target surface damage or contamination from occurring under the insulating mask.

Using a soft insulating mask provides further benefits that include less force required for contact, better sealing of the reaction area for greater field localisation, and higher resolution features.

Figures 5 and 6 are images showing the difference in resolution between a patterned substrate formed by the contact technique and contact-less technique. The pattern (i.e. fine line) in Figure 6 has a resolution of around 5µm, while the pattern (i.e. blurry line) in Figure 5 has a resolution of around 1mm.

Ultra-short pulses of current

To improve localisation of the electrochemical reaction for both contact and non-contact techniques (and improve resolution), the power supply may deliver ultra-short pulses of current during the electrochemical reaction. It is believed that the ultra-short pulse current, typically an alternating current having a pulse length in the milli-second range, assists in localising the electric field by only locally polarising/unpolarising the double layer. Ultra-short pulse current can also assist with improving reaction rate, uniformity and control over the reaction more generally.

Example

In one example, an apparatus according to the present invention including the following components can be used to form a printed circuit board (PCB).

- Stamp electrode: Including highly doped silicon wafer cut to the size of the target PCB design (100x100mm), with inert platinum layers located on both the top and the bottom surfaces. The outwardly facing surface of the silicon wafer (where the reaction takes place) has been patterned with a protruding photoresist layer. This layer acts to both confine the field, and as a standoff for setting the inter-electrode-gap uniformly across the stamp. Suitably, the photo resistant layer comprises a corrosion resistant polymer such as SU8.
- Ion source: An aqueous solution of copper sulphate precursors, pH modifiers and other additives for enhancing adhesion and surface quality.
- Substrate: ITO glass
- Current: 10s of amps.

- Potential difference and electric field parameters: IEG of 60um, deposition thickness of 30um, voltage of 2V, field intensity of 67kV/m.
- Ultra-short pulse current magnitude and time: 1us on, 10us off.

The apparatus can be used to form the PCB using the contact technique.

An ink comprising an aqueous solution of copper sulphate precursors, pH modifiers and other additives for enhancing adhesion and surface quality is applied onto the ITO glass substrate.

The stamp electrode is positioned over the substrate and lowered until the insulating layer (i.e. mask) contacts the substrate. A pressure ranging from 0.01 MPa to 10 MPa is applied to ensure that the mask conforms to the surface of the substrate.

The power supply is used to deliver a voltage of 2V to generate a field intensity of 67 kV/m. This triggers an electrochemical reaction which deposits copper onto exposed regions of the electrode around the insulating mask.

Subsequently, the stamp electrode is lifted from the substrate and the patterned substrate is washed to obtain the final product.

Figs. 7A, 7B, 7C

Fig. 7A is a side cutaway view of a stamp electrode 700 that includes an insulator substrate 702, electrodes 710, and an insulating pattern 712. In an example, the stamp electrode has two major surfaces, a first major surface 714 that is an outwardly facing surface (also referred to as a front side of the stamp electrode) and a second major surface 716 that is opposite the first major surface and referred to as a rear surface of the stamp electrode. In an example, the first major surface (e.g., the outwardly facing surface or front side) of the stamp electrode is the side of the stamp electrode that is brought into close proximity to a substrate on which conductive elements are to be formed and the second major surface (e.g., the rear side) of the stamp electrode is the opposite side of the stamp electrode.

In an example, the insulator substrate 702 may be an insulating material similar to the substrate 12 described with reference to Fig. 1 and the insulator 30 described with reference to Fig. 2. For example, the insulating substrate may be made of a flexible polymer such as polydimethylsiloxane (PDMS), or polyimide or FR4, or a stiffer insulator materials such as glass or ceramics. In an example, the substrate may be 20 μm to 2 mm thick.

Each of the electrodes 710 may be formed of a conductive material, such as a metal, including for example, copper, nickel, platinum, gold, silver, ruthenium, tungsten, or conductive non-metals such as SiN, TiN, ITO, or Si. Each electrode may be formed using, for example, metal deposition techniques such as electroplating, plasma enhanced chemical vapor deposition (PECVD), sputtering, evaporation, although other techniques are possible. In the example of Fig. 7A, there are two discrete electrodes that can be controlled independent of each other. That is, electrical current can be applied independently to each one of the two electrodes. Each of the two electrodes includes a front side portion 720, a rear side portion 722, and conductive elements 724 (e.g., conductive vias and/or conductive traces) that electrically couple the front side portion of the electrode to the rear side portion of the electrode. The front side portion of each electrode is shown in Fig. 7A at the bottom of the stamp electrode and the rear side portion of each electrode is shown in Fig. 7A at the top of the stamp electrode.

The insulating pattern 710 may be an insulating material, such as a photoresist material or hard dielectric such as SiO2, that has been deposited at the first major surface (e.g., the front or outwardly facing side) of the stamp as an insulating layer of insulating material and then patterned using photolithography or other patterning techniques such as nano-imprint lithography or direct write techniques. The insulating pattern defines features 726 that correspond to conductive elements that are to be formed on a substrate. For example, the conductive elements may be conductive pads, bumps, or traces that are formed on the substrate to conduct electricity. In an example, features that are defined by the insulating pattern may have sizes in the nanometer or micrometer range. For example, the features may define two dimensional areas (e.g., from a plan view) that correspond to conductive pads with a large range in size, ranging between 200nm and 100 mm (e.g., per side or in diameter) or conductive traces that are, for example, 20 – 100 nanometers wide or 1 – 20 micrometers

wide depending on the application. Additionally, conductive traces may have a narrow width, but can be very long, e.g., on the order of centimeter, or meters, or longer. In an example, features are defined by an absence of material of the insulating pattern such that current can pass from an electrode through an ion transport medium (such as an electrolyte) and to the target substrate on which conductive elements are to be formed. That is, areas where there is no insulating material (e.g., photoresist) are the areas that define the features of the insulating pattern.

Fig. 7B is a plan view of an example of the front side of a stamp electrode 701 that shows various features 728 that are formed by the insulating pattern at the front side of the stamp electrode. In the plan view of Fig. 7B, the features of the pattern are defined by areas that are void of the insulating material that forms the insulating pattern, e.g., void of photoresist. In an example, portions of one or more electrodes are visible at the areas of the features, e.g., the areas of the insulating pattern that are void of photoresist. As shown in Fig. 7B, various different shapes and sizes of features may be present at the front side of the stamp electrode depending on the desired application. It should be noted that the number, shapes, and layout of the features shown in Fig. 7B are for illustrative purposes only.

Fig. 7C is a plan view of an example of the rear side of a stamp electrode that shows a portion of one or more electrodes 723 of the stamp electrode. All twelve of the rear portions of the electrodes 723 are not labeled with reference numbers to preserve clarity. In the example, of Fig. 7C, the insulator substrate and portions of multiple electrodes are shown. The electrodes could be multiple different electrically isolated and individually controllable electrodes, or the electrodes could be all electrically coupled to each other by a portion or portions of the electrode that are not visible from the plan view of Fig. 7C. In an example, each electrode visible at the rear side of the stamp electrode corresponds to a different discrete conductive region of the stamp electrode. For example, the rear portion of an electrode shown at the rear side of the stamp electrode in Fig. 7C corresponds to the front portion of the same electrode at the front side of the stamp electrode.

Although an example of electrodes is described with reference to Figs. 7A, 7B, and 7C, other configurations of electrodes are possible. Additionally, the plan views shown in Figs. 7B and 7C are not necessarily the same stamp electrode. However, it is possible that the plan views

correspond to the same stamp electrode. In one example, Figs. 7A and 7B represent four electrically independent electrodes, electrodes 1, 2, 3, and 4. In particular, Fig. 7A shows four features, features 1, 2, 3, and 4, defined by the insulating pattern that expose the front side portion of the four electrically independent electrodes and Fig. 7B shows the rear side of the stamp electrode that shows the rear portion of the same four electrodes, 1, 2, 3, and 4. As illustrated in Figs. 7B and 7C, the front side portion of an electrode is not necessarily spatially aligned with the rear side portion of the same electrode but the front side portion and the rear side portion of the electrode are electrically coupled to each other, e.g., through vertical and/or horizontal conductive traces (not shown). In an example, the features formed by the insulating pattern may define three-dimensional areas that include, for example, length and width dimensions (e.g., from a plan view, Fig. 7B) and a depth dimension (e.g., from a side view, Fig. 7A).

Figs. 8A/8B

As described above, a stamp electrode may include multiple discrete conductive regions, wherein the electrical potential and current of each region can be independently modulated. Fig. 8A is a plan view of an example of the front side of a stamp electrode 800 that shows multiple discrete conductive regions 830, with each discrete conductive region having various features 826 that are formed by the insulating pattern at the front side of the stamp electrode. In the plan view of Fig. 8A, there are eight discrete conductive regions and the features of the insulating pattern within each discrete conductive region are defined by areas that are void of the insulating pattern, e.g., void of photoresist, such that portions of one or more electrodes are exposed at the areas of the features. The areas in the plan view of Fig. 8A that are not pattern features are covered by an insulating material such as photoresist. As shown in Fig. 8A, various different shapes and sizes of features may be present on the front side of the stamp electrode depending on the desired application. Although different features are shown in each conductive region of the stamp electrode, the features do not have to be divided by conductive region.

Fig. 8B is a plan view of an example of the rear side of the stamp electrode 800 from Fig. 8A that shows a portion of the electrodes 820 of the stamp electrode. In the example of Fig. 8B, the substrate and a portion of multiple electrodes are shown and the discrete conductive

regions 830 align with the discrete conductive regions 830 shown in Fig. 8A such that the front side portion of an electrode and the rear side portion of the same electrode are electrically coupled to each other by, for example, vertical and/or horizontal conductive elements (not shown). In the example of Fig. 8B, one electrode corresponds to one discrete conductive region, such that electrical potential and current is individually controllable within each discrete conductive region. For example, one electrode in one conductive region is used to apply electrical potential and current to one conductive region such that the conductive elements that correspond to the pattern features can be formed on a substrate. In the example of Figs. 8A and 8B, the discrete conductive regions 830 are vertically aligned with each other although in other examples, the rear portion of an electrode is not vertically aligned with the front portion of the electrode.

Fig. 9

In some examples, the footprint of an electrode at the front side of a stamp electrode is much larger than the sizes of the conductive elements (e.g., bumps and/or traces) that are to formed on the substrate based on current applied from the electrode. Fig. 9 is a side cutaway view of a stamp electrode 900 that includes an insulator substrate 902, two electrodes 910, and an insulating pattern 912. In the example, the footprint of each of the two electrodes is much larger than the size of the features 926 that are defined by the insulating pattern. In an example, features that are defined by the insulating pattern may have sizes in the nanometer or micrometer range. For example, the features may include conductive pads or conductive traces that are 20 – 100 nanometers wide or 1 – 20 micrometers wide while the front side portion of the electrode has a footprint that is larger than the size of the features, and could be as large as multiple centimeters squared. Additionally, conductive traces may have a narrow width, but can be very long, e.g., on the order of centimeter, or meters, or longer.

As described above, the stamp electrode 900 described with reference to Fig. 9 has two major surfaces, a first major surface 916 that is an outwardly facing surface (also referred to as a front side) and a second major surface 914 that is opposite the first major surface and referred to as a rear surface. The electrodes 910 are two discrete electrodes that can be controlled independent of each other. Each of the two electrodes includes a front side portion 922, a rear side portion 720, and a conductive via 724 that electrically couples the front side portion

to the rear side portion. In an example, the two electrodes have rectangular footprints at both the front side and rear side of the stamp electrode. In the example of Fig. 9, for each electrode, the area of the footprint of the portion of the electrode at the front side of the stamp electrode is much larger than the area of the footprint of the portion of the electrode at the rear side of the stamp electrode, although in other examples, the reverse could be true. Further, although the portion of the electrode at the front side of the stamp electrode is vertically aligned with the portion of the electrode at the rear side of the stamp electrode in the example of Fig. 9, the front side and rear side portions of the same electrode do not have to be vertically aligned with each other. For example, the portion of the electrode at the front side of the stamp electrode can be electrically coupled to the portion of the electrode at the rear side of the stamp electrode through vertical and/or horizontal conductive traces.

Fig. 10

Fig. 10 is a side cutaway view of an example of a stamp electrode 1000 similar to the examples of electrode 10 and electrode 11 shown in Fig. 2. In the example of Fig. 10, there are two channels 1040 that pass through the insulator substrate 1002 from the front side of the stamp electrode to the rear side of the stamp electrode near an electrode 1010. In an example, fluid may move in either direction through the channels. In one example, fluid is pumped through a first one of the channels into a space 1042 between the stamp electrode 1000 and a substrate 1044 and fluid exits the space between the stamp electrode and the substrate through a second one of the channels.

Figs. 11A/11B

Fig. 11A is a plan view of an example of the front side of a stamp electrode 1100 that shows multiple features 1126 formed by the insulating pattern, one end 1141 of each of four fluid channels, and an outline of a front side portion 1122 of an electrode. Fig. 11B is a plan view of an example of the rear side of the stamp electrode 1100 from Fig. 11A that shows the opposite end 1143 of each of the four fluid channels as well as a rear side portion 1120 of the electrode that is visible at the rear side of the stamp electrode. Fig. 11B also shows an outline of the front side portion 1122 of the electrode that is at the front side of the stamp electrode,

which would not be visible at the front side of the stamp electrode. In the example of Figs. 11A and 11B, fluid channels are located around a perimeter of the electrode although this is not a requirement. A fluid channel, or multiple fluid channels, may be positioned relative to the features 1126 in other ways that are designed to enhance performance of the process of forming the conductive elements on the substrate. The fluid channels may be similar to the fluid channels in the electrode 10 and electrode 11 shown in Fig. 2 and/or to the fluid channels described with reference to Fig. 10.

Fig. 12

Fig. 12 is a side cutaway view of an example of a stamp electrode 1200 similar to the example described with reference to Figs. 10, 11A, and 11B. In the example of Fig. 12, there are two channels 1240 that pass through the insulator substrate 1202 from the front side of the stamp electrode to the rear side of the stamp electrode and that pass through the front side portion 1222 of the electrode that is at the front side of the stamp electrode. In an example, fluid may move in either direction through the channels. In one example, fluid is pumped through a first one of the channels into a space 1242 between the stamp electrode 1200 and the substrate 1244 and fluid exits the space between the stamp electrode and the substrate through a second one of the channels.

Fig. 13

Fig. 13 is a plan view of an example of the front side of a stamp electrode 1300 that shows one end 1341 of multiple fluid channels and an outline of the front side portion 1322 of two electrodes. For clarity, the plan view of the front side of the stamp electrode in Fig. 13 does not include features that may be formed by an insulating pattern. In the example of Fig. 13, a variety of possibilities for fluid channels are shown. With respect to the shape of the fluid channels, the fluid channels are shown with a circular cross section and with a linear cross section although other cross sectional shapes are possible. With respect to the location of the fluid channels, a fluid channel may be located outside of the footprint of the front side portion of an electrode (e.g., as shown in Fig. 10), or a fluid channel may be located within the footprint of the front side portion of an electrode (e.g., as shown in Fig. 12). In an example, the fluid channels are configured to enable an ion source, such as an ink, to be delivered close

to the location of the features (not shown) in the insulating pattern and/or to provide a nearby exit path for excess fluid when the electrode stamp is brought into close proximity to a substrate on which the conductive elements are to be formed.

Figs. 14A, 14B, 14C

Fig. 14A is a side cutaway view of a stamp electrode 1400 that includes an insulator substrate 1402, two electrodes 1410, and an insulating pattern 1412 that defines features 1426. In an example, the stamp electrode has two major surfaces, a first major surface that is an outwardly facing surface (also referred to as a front side of the stamp electrode) and a second major surface that is opposite the first major surface and referred to as a rear surface of the stamp electrode. Each of the two electrodes has a front side portion 1422, a rear side portion 1420, and conductive elements 1424 that electrically couple the front side portion of the electrode to the rear side portion of the electrode. As shown in Fig. 14A, the front side portions of the electrodes are electrically coupled to the rear side portions of the respective electrodes by a combination of vertical vias and horizontal traces.

Fig. 14B is a plan view of an example of the front side of a stamp electrode 1401 that shows the front side portion 1422 of four electrodes and an outline of the rear side portion 1420 of the four electrodes and Fig. 14C is a plan view of an example of the rear side of the stamp electrode from Fig. 14B that shows the rear side portion 1420 of the same four electrodes of the stamp electrode and an outline of the front side portion 1422 of the four electrodes. Note that the plan view of the front side of the stamp electrode does not show the insulating pattern and corresponding features to maintain clarity of the figure. In the example shown in Figs. 14B and 14C, the front side portions of the electrodes and the respective rear side portions of the electrodes may be electrically coupled to each other by conductive elements 1424 such as those described with reference to Fig. 14A. Conductive elements that electrically couple the front side portions of the electrodes to the rear side portions of the electrodes are shown with dashed lines in Figs. 14B and 14C. As illustrated in Figs. 14A – 14C, the front side portion of an electrode may be offset from the rear side portion of the electrode from a plan view perspective, which provides flexibility in the layout of the electrodes of a stamp electrode that may include many different electrodes that are individually controllable. In the example described with reference to Figs. 14A – 14C, the electrodes 1, 2, 3, and 4 each correspond to

discrete conductive regions that are electrically insulated from each other. That is, electrical current does not pass between the four different electrodes that correspond to four discrete conductive regions. In the example of Figs. 14A – 14C, the stamp electrode 1400 shown in Fig. 14A is not necessarily the same stamp electrode 1401 as that shown in Figs. 14B and 14C but it may be the same stamp electrode.

Figs. 15A, 15B, 15C

Fig. 15A is a side cutaway view of a stamp electrode 1500 that includes an insulator substrate 1502, two electrodes 1510, and an insulating pattern 1512 that defines features 1526. In an example, the stamp electrode has two major surfaces, a first major surface that is an outwardly facing surface (also referred to as a front side of the stamp electrode) and a second major surface that is opposite the first major surface and referred to as a rear surface of the stamp electrode. Each of the two electrodes has a front side portion 1522, a rear side portion 1520, and a conductive element 1524 that electrically couples the front side portion of the electrode to the rear side portion of the electrode although the rear side portion and corresponding conductive elements for one of the electrodes are not visible in the side cutaway view of Fig. 15A.

Fig. 15B is a plan view of an example of the front side of a stamp electrode 1501 that shows features 1526 that are defined by an insulating pattern and an outline of the front side portion 1522 of four electrodes of the stamp electrode and Fig. 15C is a plan view of an example of the rear side of the stamp electrode from Fig. 15B that shows the rear side portion 1520 of the same four electrodes of the stamp electrode and an outline of the corresponding front side portion 1522 of the four electrodes. In the example shown in Figs. 15B and 15C, the front side portions of the electrodes and the respective rear side portions of the electrodes may be electrically coupled to each other by conductive vias such as that described with reference to Fig. 15A. In an example, the conductive vias that electrically couple the front side portions of the electrodes to the rear side portions of the electrodes are vertical vias that are not shown in Figs. 15B and 15C. As illustrated in Figs. 15A – 15C, the front side portion 1520 of an electrode may be offset from the rear side portion 1522 of the electrode from a plan view perspective, which provides flexibility in the layout of the electrodes of a stamp electrode that may include many different electrodes that are individually controllable. In the example of

Figs. 15A – 15C, the stamp electrode 1500 shown in Fig. 15A is not necessarily the same stamp electrode 1501 as that shown in Figs. 15B and 15C but it may be the same stamp electrode.

Although specific embodiments of the invention have been described and illustrated, the invention is not to be limited to the specific forms or arrangements of parts so described and illustrated. The scope of the invention is to be defined by the claims appended hereto and their equivalents.

What is Claimed Is:

1. An apparatus for forming conductive elements on a substrate, the apparatus comprising:

an insulator substrate;

an electrode integrated with the insulator substrate; and

an insulating pattern formed over the electrode, wherein the insulating pattern defines features that correspond to the conductive elements that are to be formed on the substrate.

2. The apparatus of claim 1, wherein the electrode has a two-dimensional footprint at an outwardly facing surface of the apparatus, and wherein multiple features are located within the two-dimensional footprint at the outwardly facing surface of the apparatus.

3. The apparatus of claim 1, wherein the electrode has a two-dimensional footprint at a front side of the apparatus, and wherein multiple features are located within the two-dimensional footprint at the front side of the apparatus.

4. The apparatus of claim 1, wherein the electrode has a front side portion with a two-dimensional area at a front side of the apparatus and a rear side portion with a two-dimensional area at a rear side of the apparatus, and wherein the two-dimensional area of the rear side portion of the electrode is greater than the two-dimensional area of the front side portion of the electrode.

5. The apparatus of claim 1, wherein the insulating pattern includes an insulating layer of insulating material, wherein the features are formed via photolithography.

6. The apparatus of claim 1, wherein the features have dimensions on the order of micrometers.

7. The apparatus of claim 1, wherein the features have dimensions on the order of nanometers.

8. The apparatus of claim 1, further including multiple electrodes, wherein the electrodes correspond to discrete conductive regions at an outwardly facing side of the apparatus.

9. The apparatus of claim 1, further including multiple electrodes, wherein the electrodes correspond to discrete conductive regions at a front side of the apparatus.

10. The apparatus of claim 1, further including multiple electrodes, wherein the electrodes correspond to discrete conductive regions at an outwardly facing surface of the apparatus, and wherein the electrodes are configured to be independently modulated with electrical potential and current.

11. The apparatus of claim 1, further including multiple electrodes, wherein the electrodes correspond to discrete conductive regions at a front side of the apparatus, and wherein the electrodes are configured to be independently modulated with electrical potential and current.

12. The apparatus of claim 1, further including a fluid channel within the insulator substrate, wherein an end of the fluid channel is at an outwardly facing side of the apparatus.

13. The apparatus of claim 1, further including a fluid channel that passes through the insulator substrate from a front side of the apparatus to a rear side of the apparatus, wherein the fluid channel is configured to provide an ion source to the front side of the apparatus.

14. The apparatus of claim 1, further including a fluid channel that passes through the insulator substrate, wherein the fluid channel is configured to provide an ion source to the outwardly facing side of the apparatus near the electrode.

15. An apparatus for forming conductive elements on a substrate, the apparatus comprising:

an insulator substrate;

electrodes integrated with the insulator substrate, wherein the electrodes correspond to discrete conductive regions of the apparatus; and

an insulating pattern formed over the electrodes, wherein the insulating pattern defines features that correspond to the conductive elements that are to be formed on the substrate.

16. The apparatus of claim 15, wherein each of the electrodes has a front side portion with a two-dimensional area at a front side of the apparatus and a rear side portion with a two-dimensional area at a rear side of the apparatus, and wherein each of the electrodes is individually controllable.

17. An apparatus for forming a high resolution patterned substrate for a device, the apparatus comprising:

a stamp electrode that is configured to form a pattern on a substrate, the electrode having an outwardly-facing surface on which is applied a mask having a predetermined pattern, wherein the stamp electrode is further configured to confine the electrochemical reaction to regions of the substrate less than 200μm wide or deliver high current densities of greater than 10 kA/dm2 (or greater than 1 A/mm2) to the selected regions of the substrate during the electrochemical reaction;

an ion source to supply ions for forming a pattern on a substrate; and

a power supply to initiate movement of ions between the ion source and the substrate and an electrochemical reaction to form the pattern on the substrate, wherein the pattern is the same as or inverse to the predetermined pattern of the mask.

18. A method of forming a high resolution patterned substrate for a device using an apparatus comprising a stamp electrode having an outwardly-facing surface on which is applied a mask having a predetermined pattern; an ion source to supply ions for forming a pattern on a substrate; and a power supply to initiate movement of ions between the ion source and the substrate and an electrochemical reaction to form the pattern on the substrate, the method including:

providing a substrate;

positioning the stamp electrode relative to the substrate to enable movement of ions between the ion source and the substrate; and

delivering high current densities of greater than 10 kA/dm2 (or greater than 1 A/mm2) to the selected regions of the substrate during the electrochemical reaction to generate an electric field and/or confining the electrochemical reaction to regions of the substrate less than 200 μm wide to form the pattern on the substrate, wherein the pattern is the same or inverse to the predetermined pattern of the mask.