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(54) **PATTERN TRANSFER BY SOLID STATE ELECTROCHEMICAL STAMPING**

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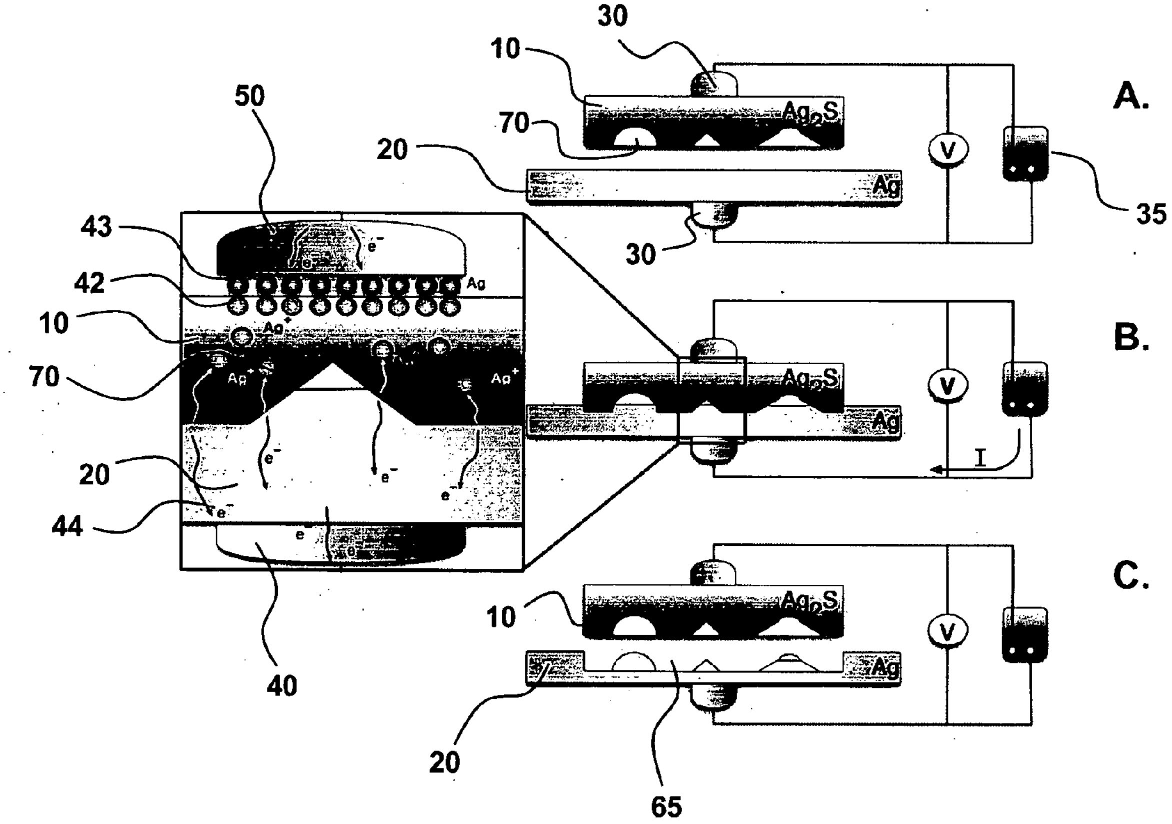
(57) **ABSTRACT**

The present invention provides an electrochemical fabrication platform for making structures, arrays of structures and functional devices having selected nanosized and/or microsized physical dimensions, shapes and spatial orientations. Methods, systems and system components of the present invention use an electrochemical stamping tool for generating patterns of relief and/or recessed features exhibiting excellent reproducibility, pattern fidelity and resolution on surfaces of solid state ionic conductors and in metal. Electrochemical stamping tools of the present invention are capable high throughput patterning of large substrate areas and, thus, enable a robust and commercially attractive manufacturing pathway to a range of functional systems and devices including nano- and micro-electromechanical systems, sensors, energy storage devices and integrated electronic circuits.



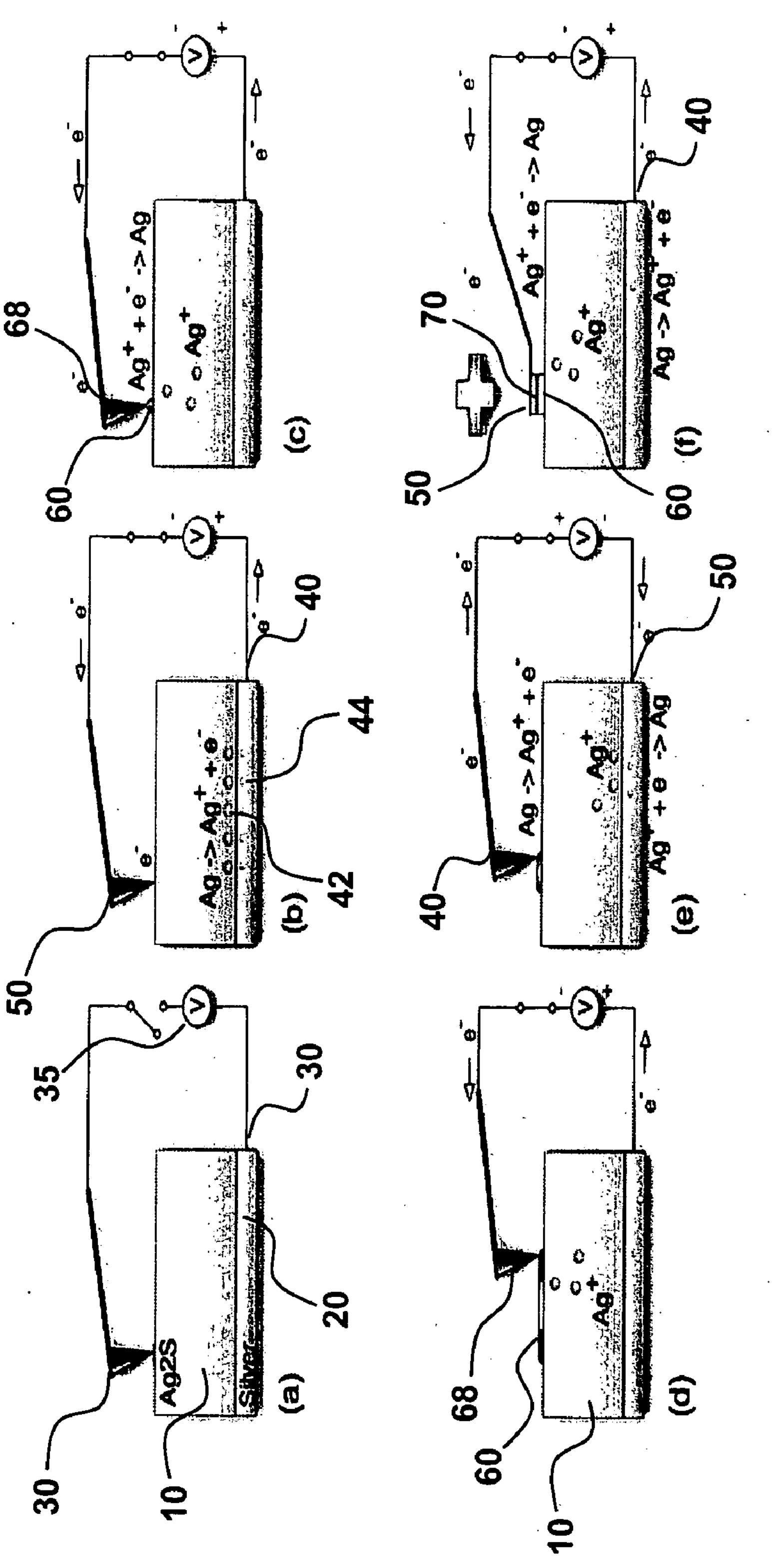

30
10
Ag2S
Silver
20
30
35
V
(a)
50
e⁻
Ag -> Ag⁺ + e⁻
42
44
40
(b)
60
68
Ag⁺ + e⁻ -> Ag
Ag⁺
(c)
10
60
68
Ag⁺
(d)
40
Ag -> Ag⁺ + e⁻
Ag⁺
Ag⁺ + e -> Ag
50
(e)
50
70
60
Ag⁺ + e⁻ -> Ag
Ag⁺
Ag -> Ag⁺ + e
40
(f)

Fig. 1

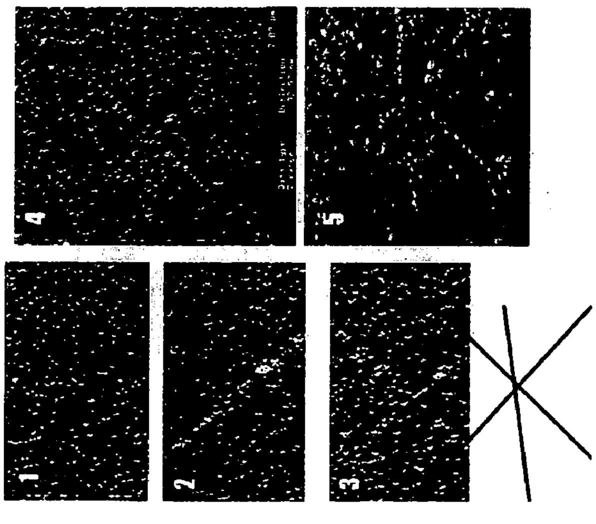

1
2
3
4
5

Fig. 2

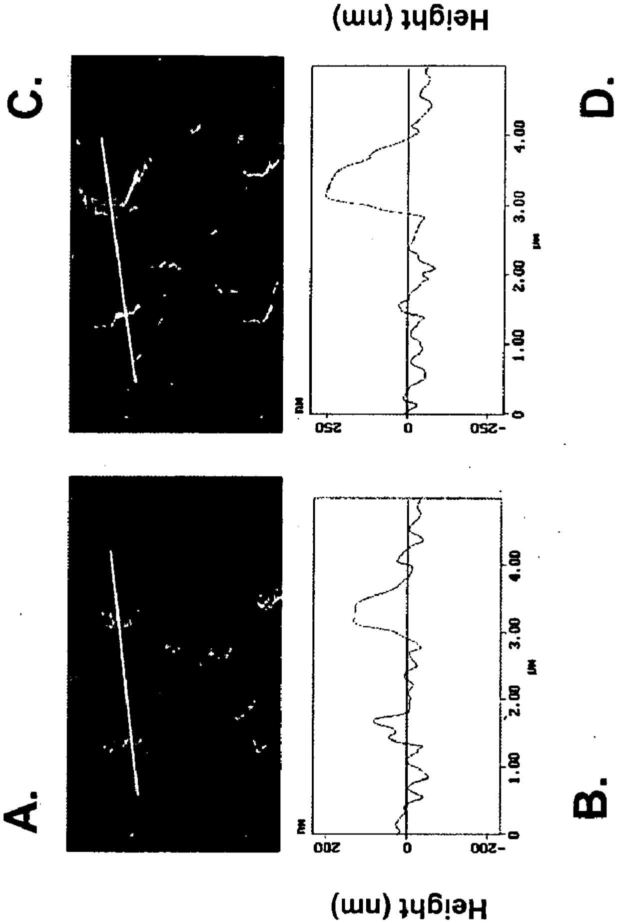

A.
B.
C.
D.
Height (nm)
Height (nm)
200
0
-200
250
0
-250
0
1.00
2.00
3.00
4.00
µm
nm

Fig. 3

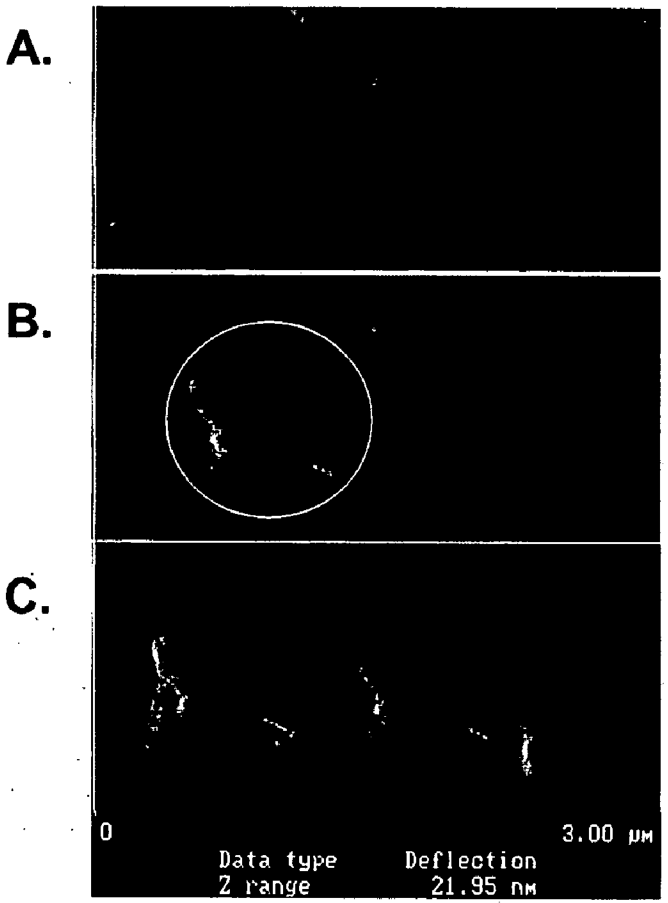


Fig. 4

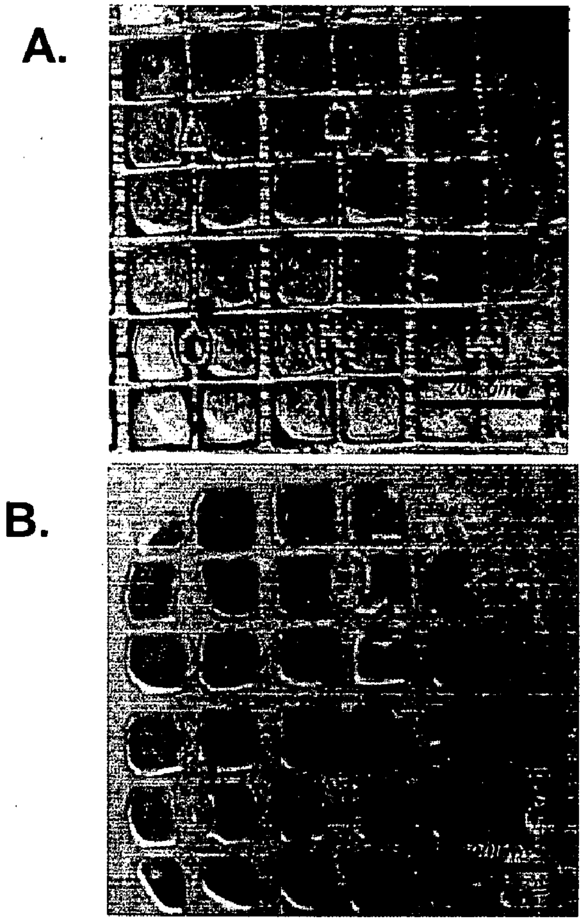


Fig. 5

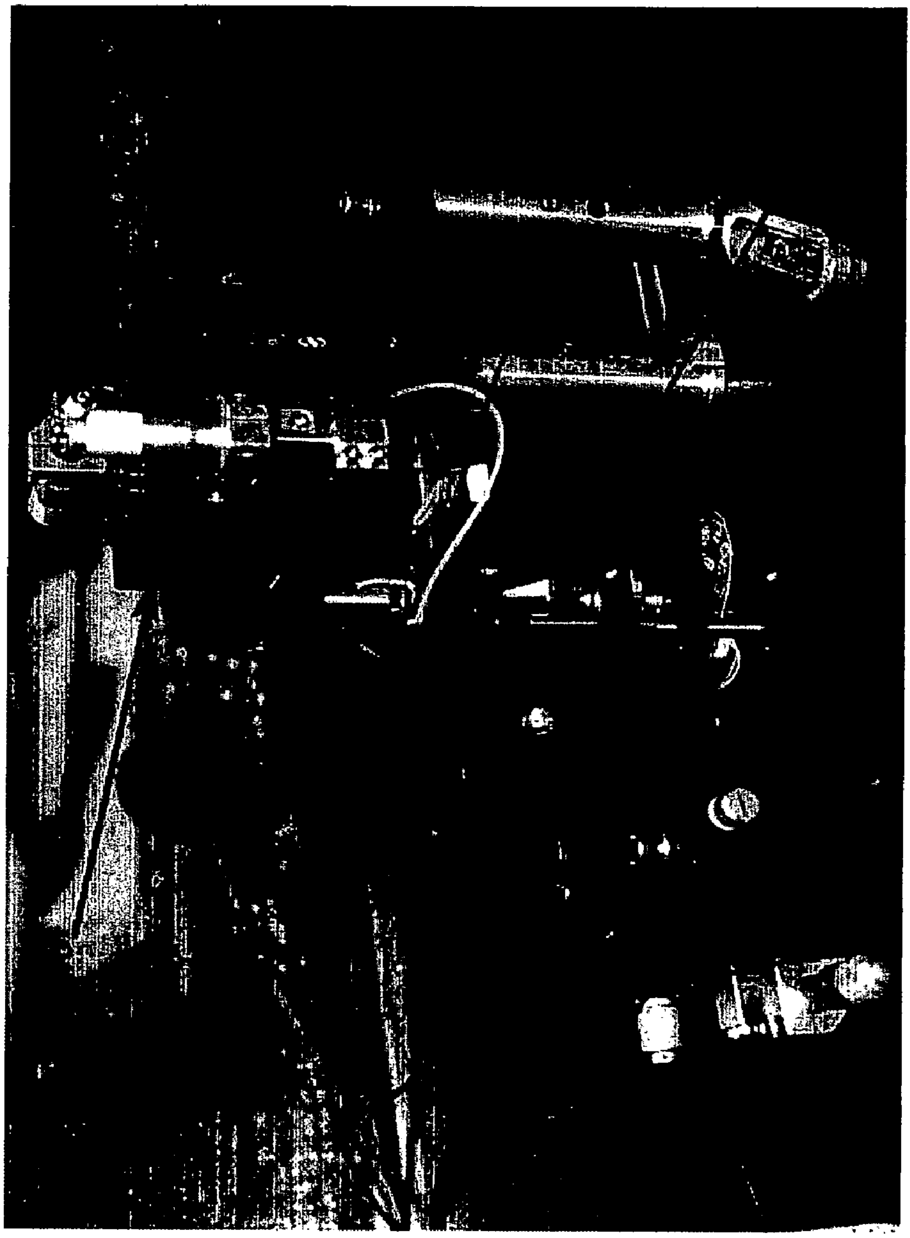


Fig. 6

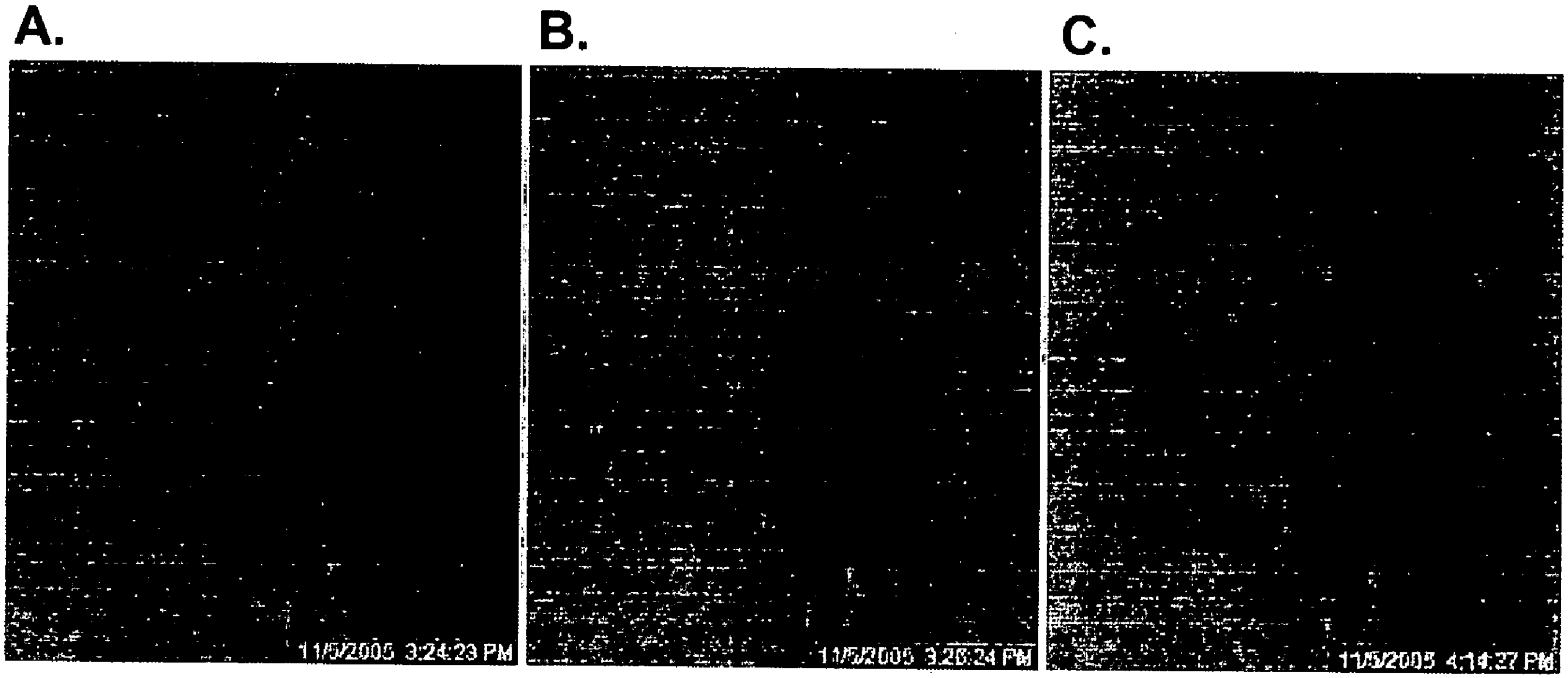


Fig. 7

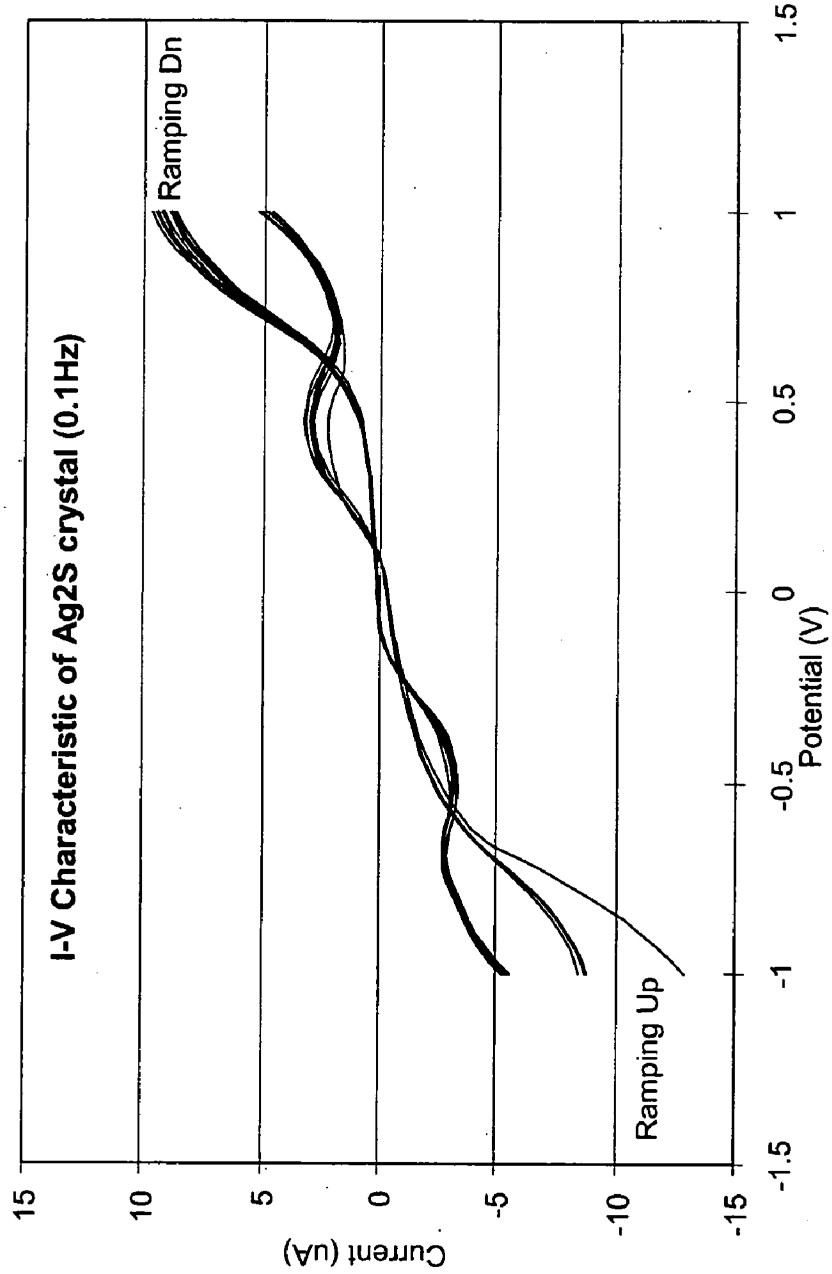

I-V Characteristic of Ag2S crystal (0.1Hz)
Current (uA)
15
10
5
0
-5
-10
-15
Potential (V)
-1.5
-1
-0.5
0
0.5
1
1.5
Ramping Dn
Ramping Up

Fig. 8

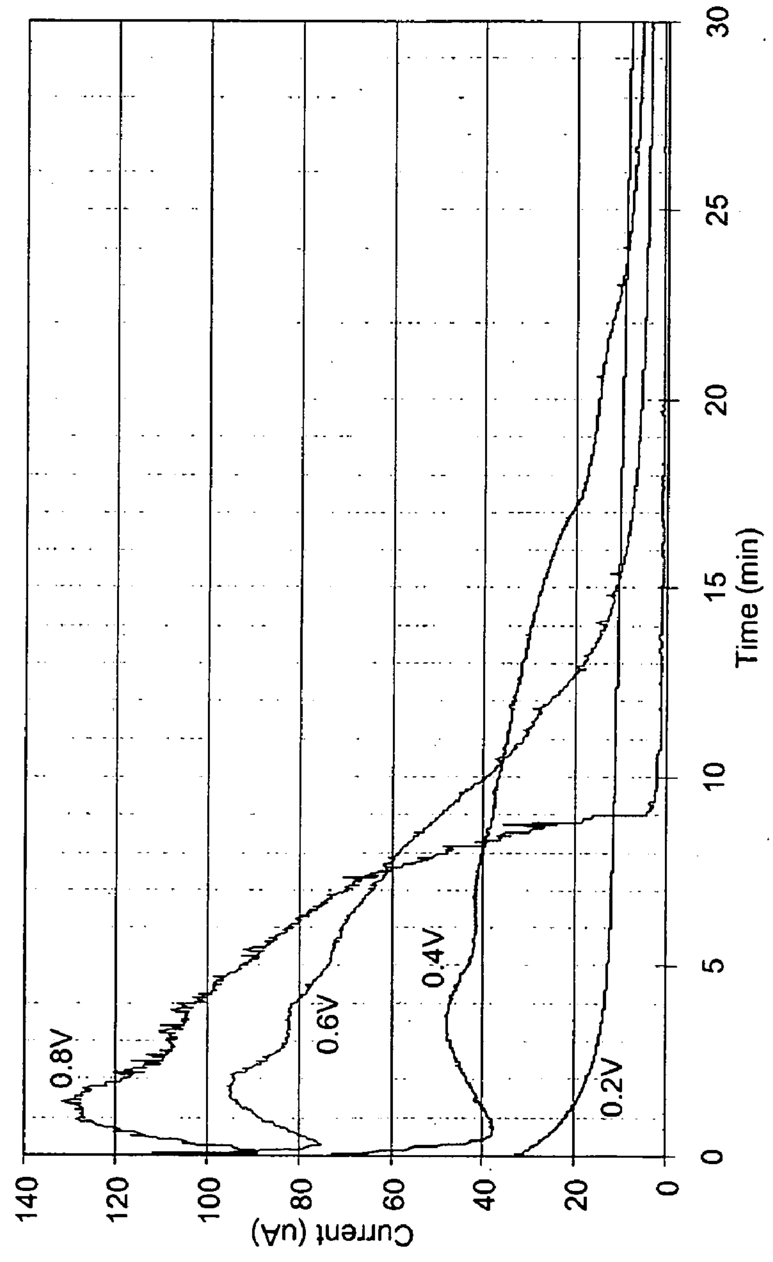

140
120
100
80
60
40
20
0
Current (uA)
0
5
10
15
20
25
30
Time (min)
0.8V
0.6V
0.4V
0.2V

Fig. 9

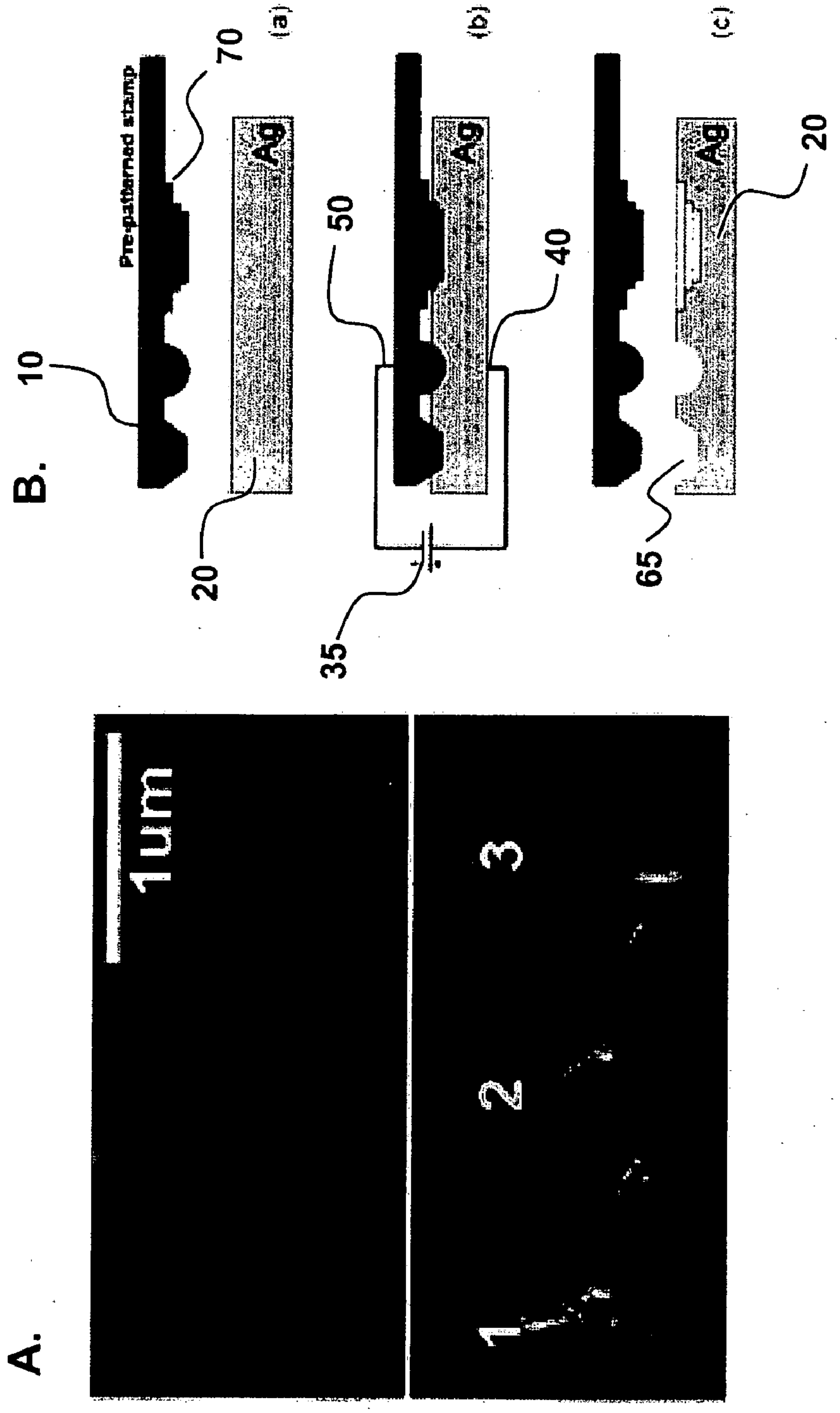

B.
10
Pre-patterned stamp
70
(a)
Ag
20
50
40
(b)
35
Ag
(c)
Ag
20
65
A.
1um
1
2
3

Fig. 10

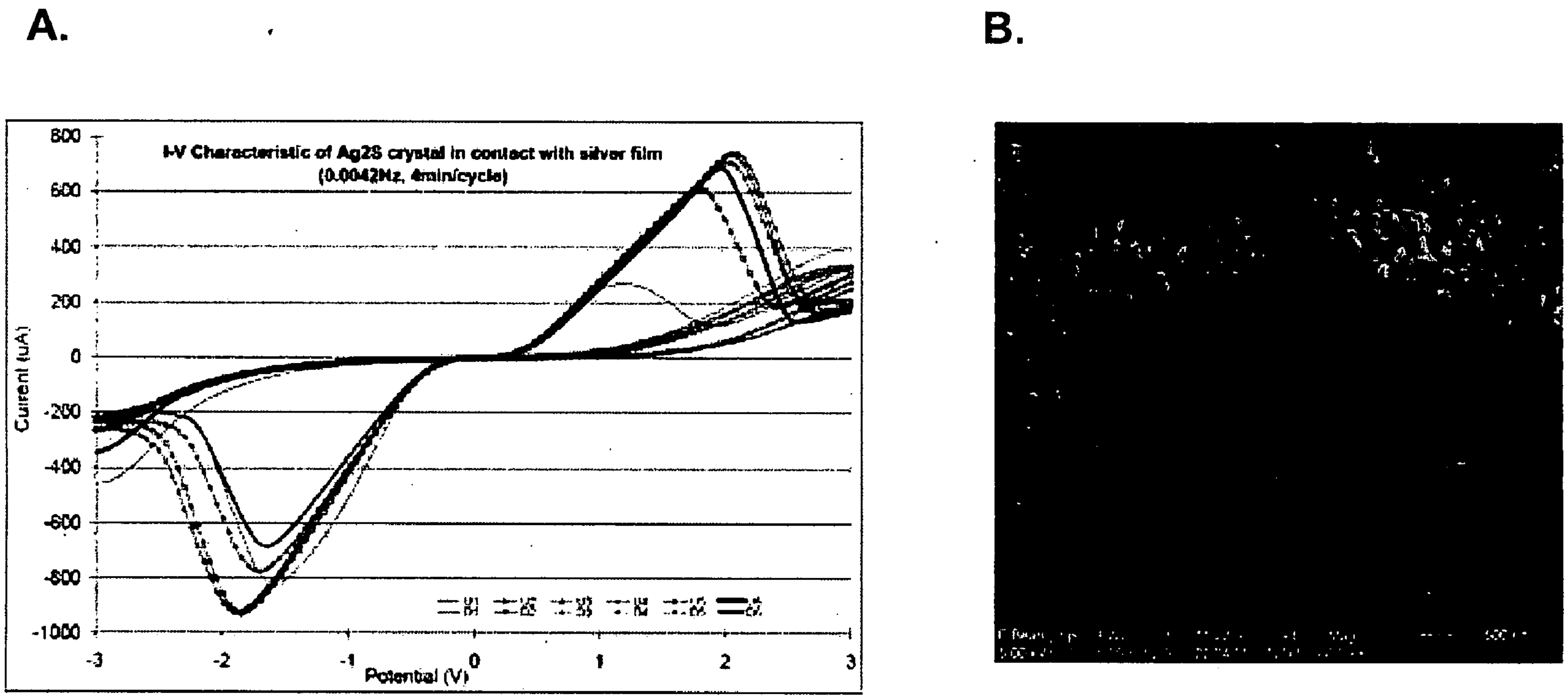

A.
I-V Characteristic of Ag2S crystal in contact with silver film
(0.0042Hz, 4min/cycle)
800
600
400
200
0
-200
-400
-600
-800
-1000
Current (uA)
-3
-2
-1
0
1
2
3
Potential (V)
B.

Fig. 11

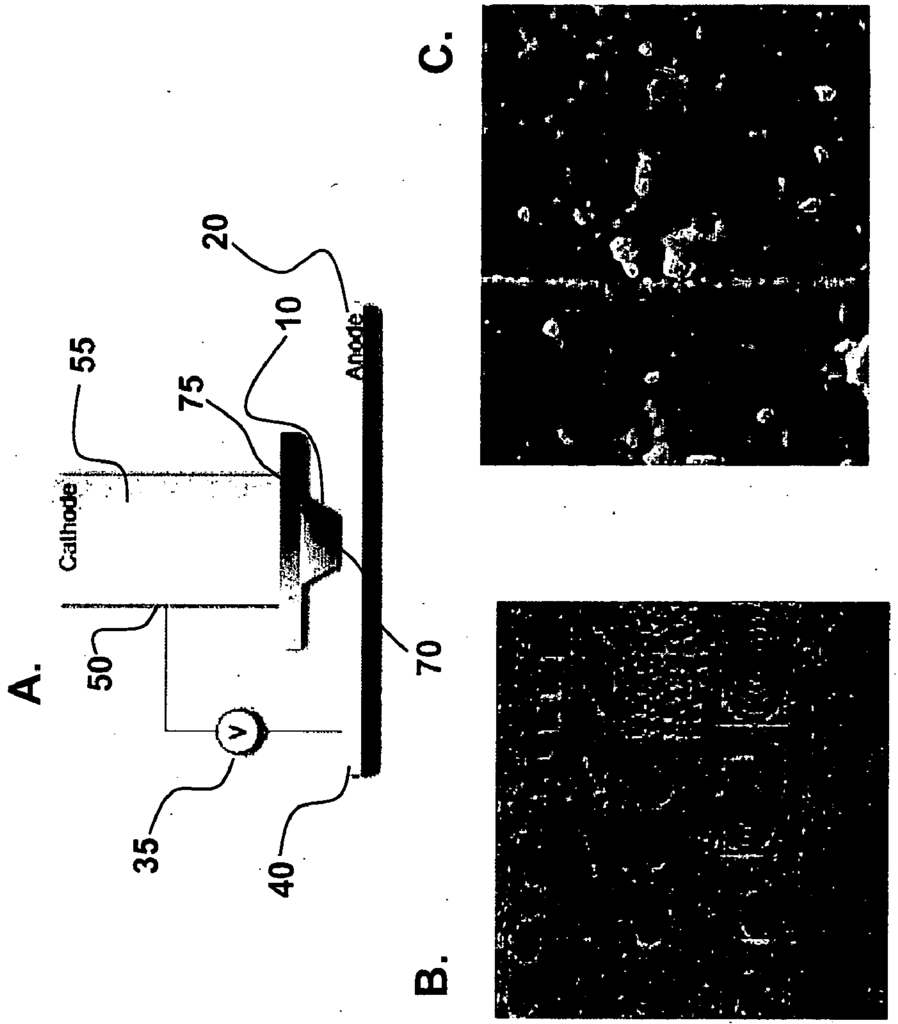
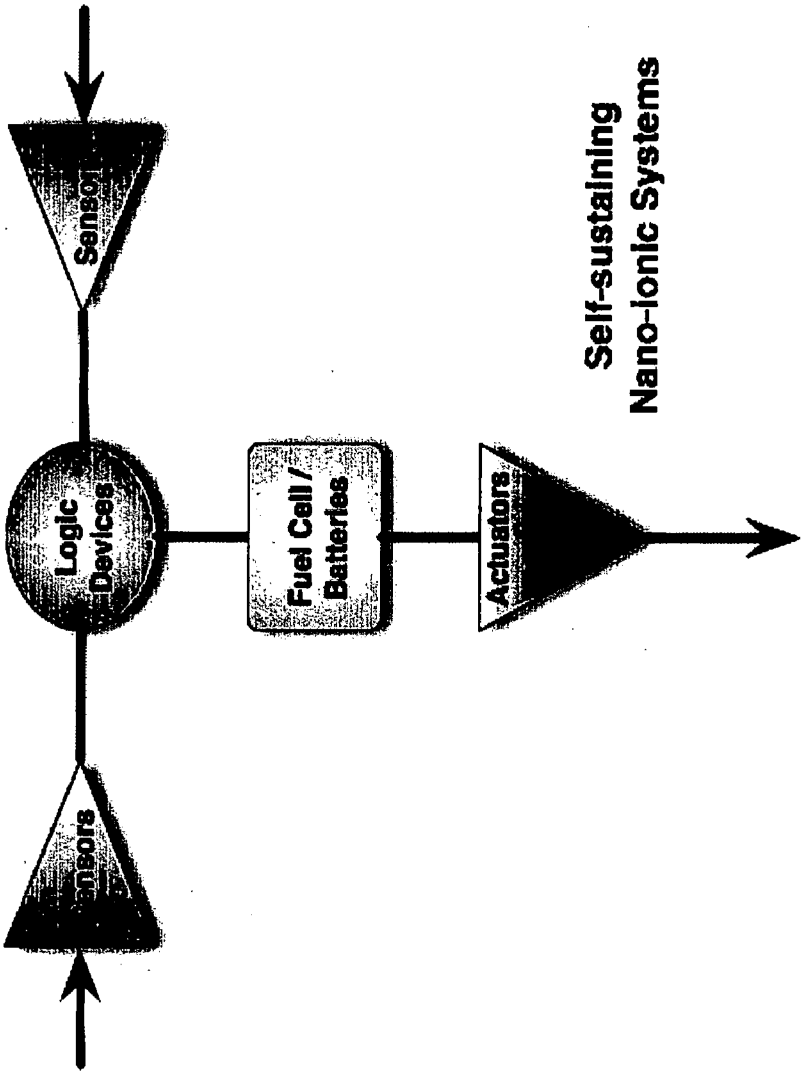


Fig. 12



Self-sustaining Nano-Ionic Systems

Fig. 13

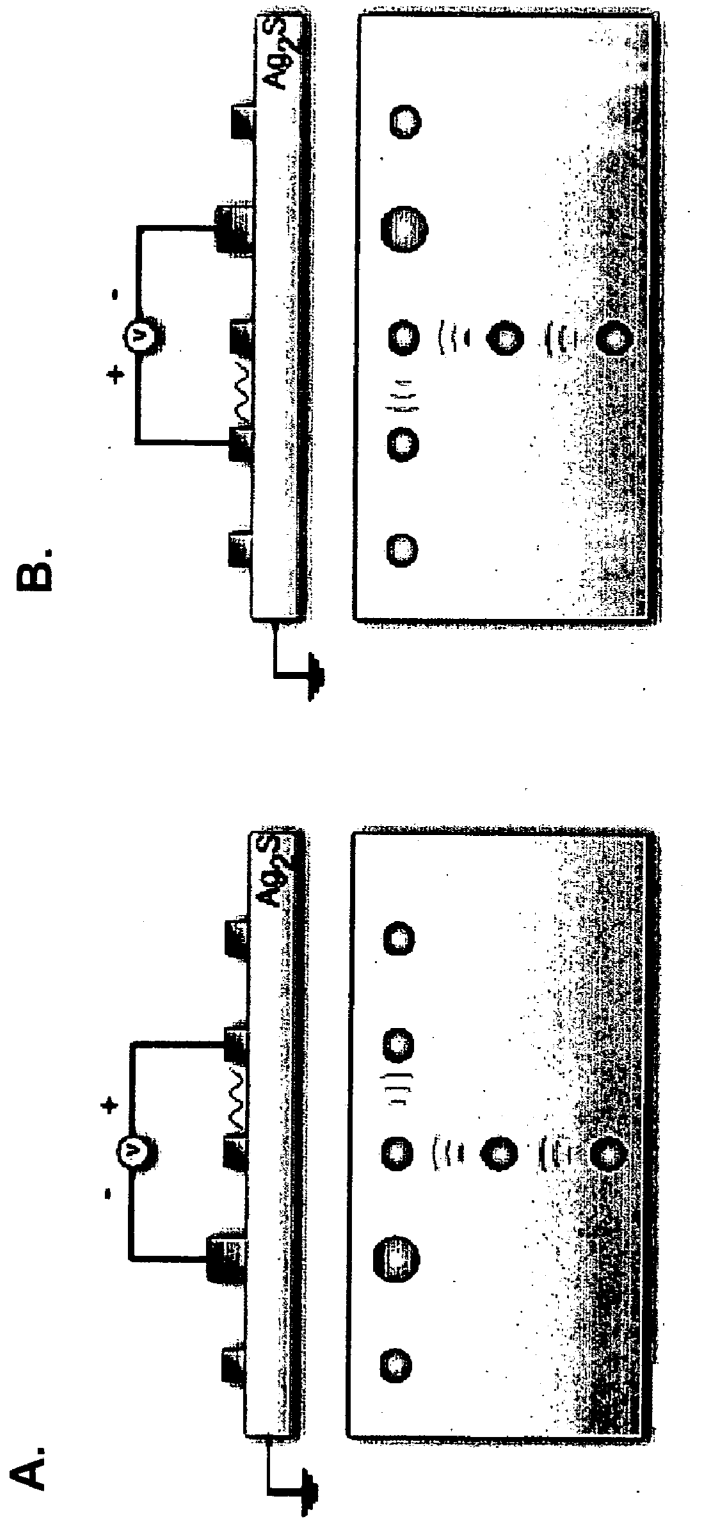


Fig. 14

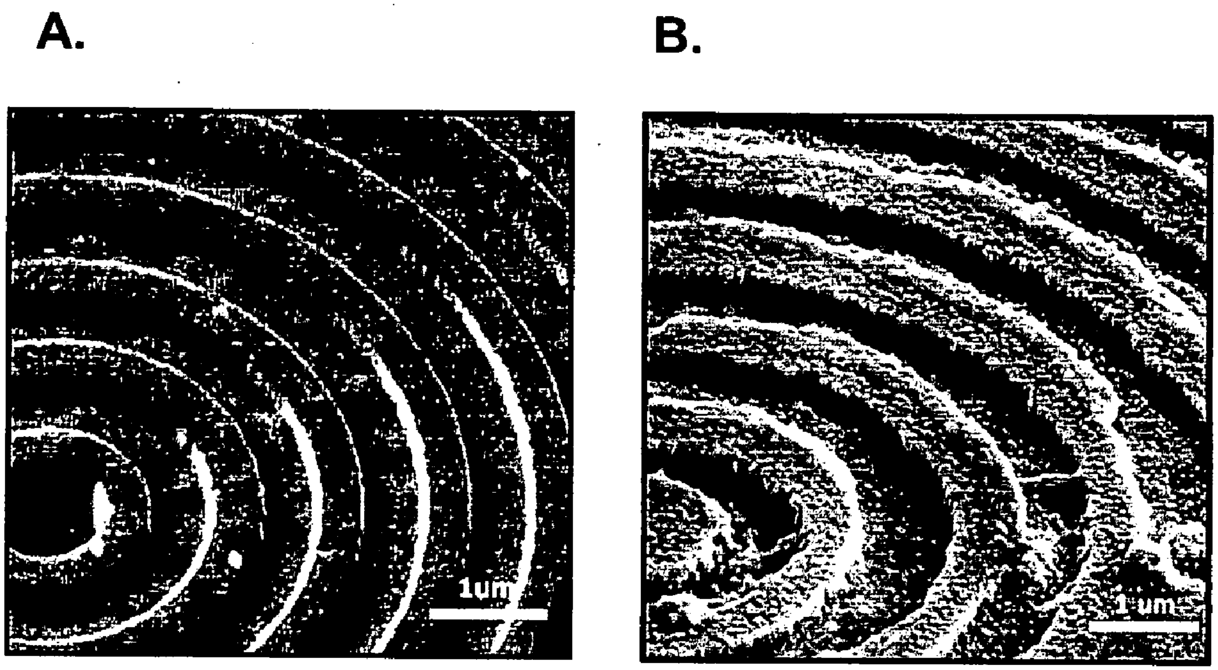


Fig. 15

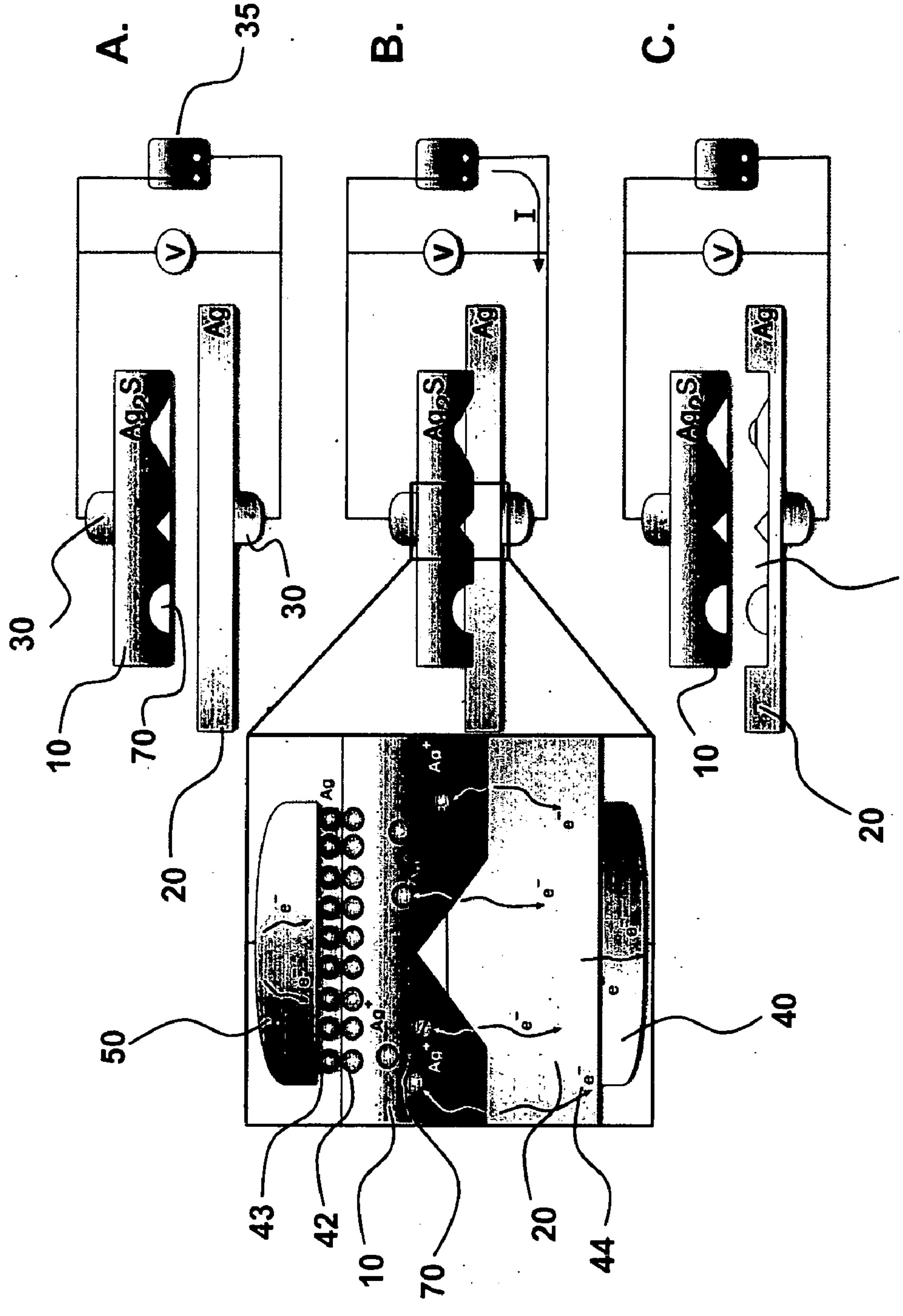


Fig. 16

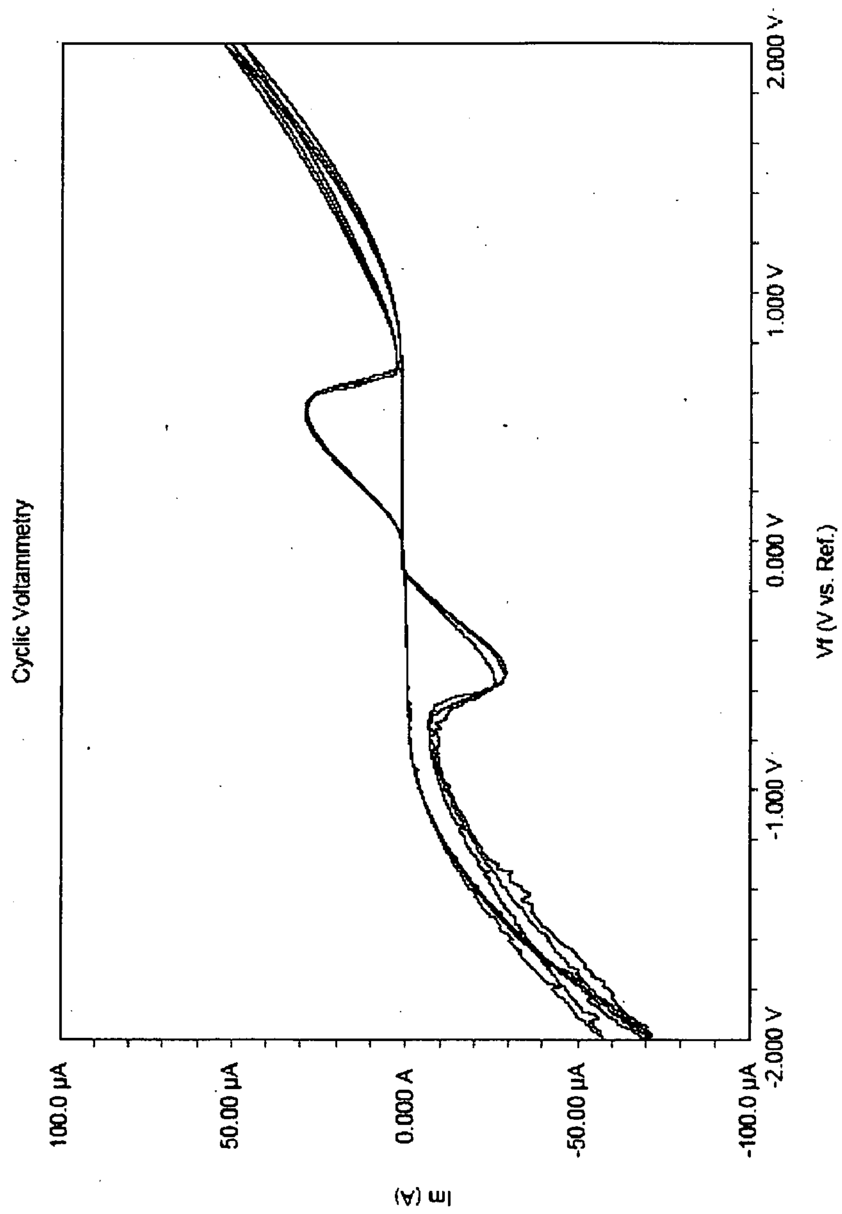

Cyclic Voltammetry
100.0 µA
50.00 µA
0.000 A
-50.00 µA
-100.0 µA
Im (A)
-2.000 V
-1.000 V
0.000 V
1.000 V
2.000 V
Vf (V vs. Ref.)

Fig. 17

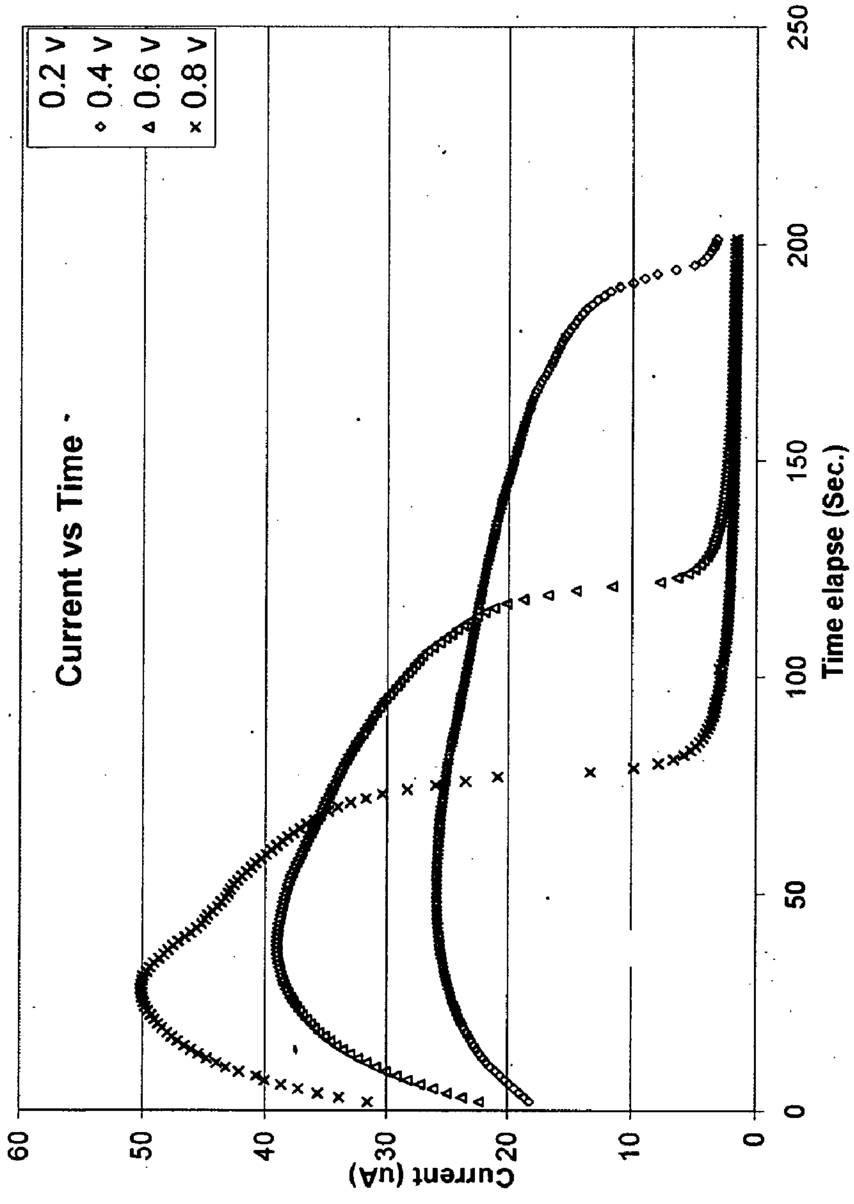

Current vs Time
0.2 v
0.4 v
0.6 v
0.8 v
Current (uA)
60
50
40
30
20
10
0
Time elapse (Sec.)
0
50
100
150
200
250

Fig. 18

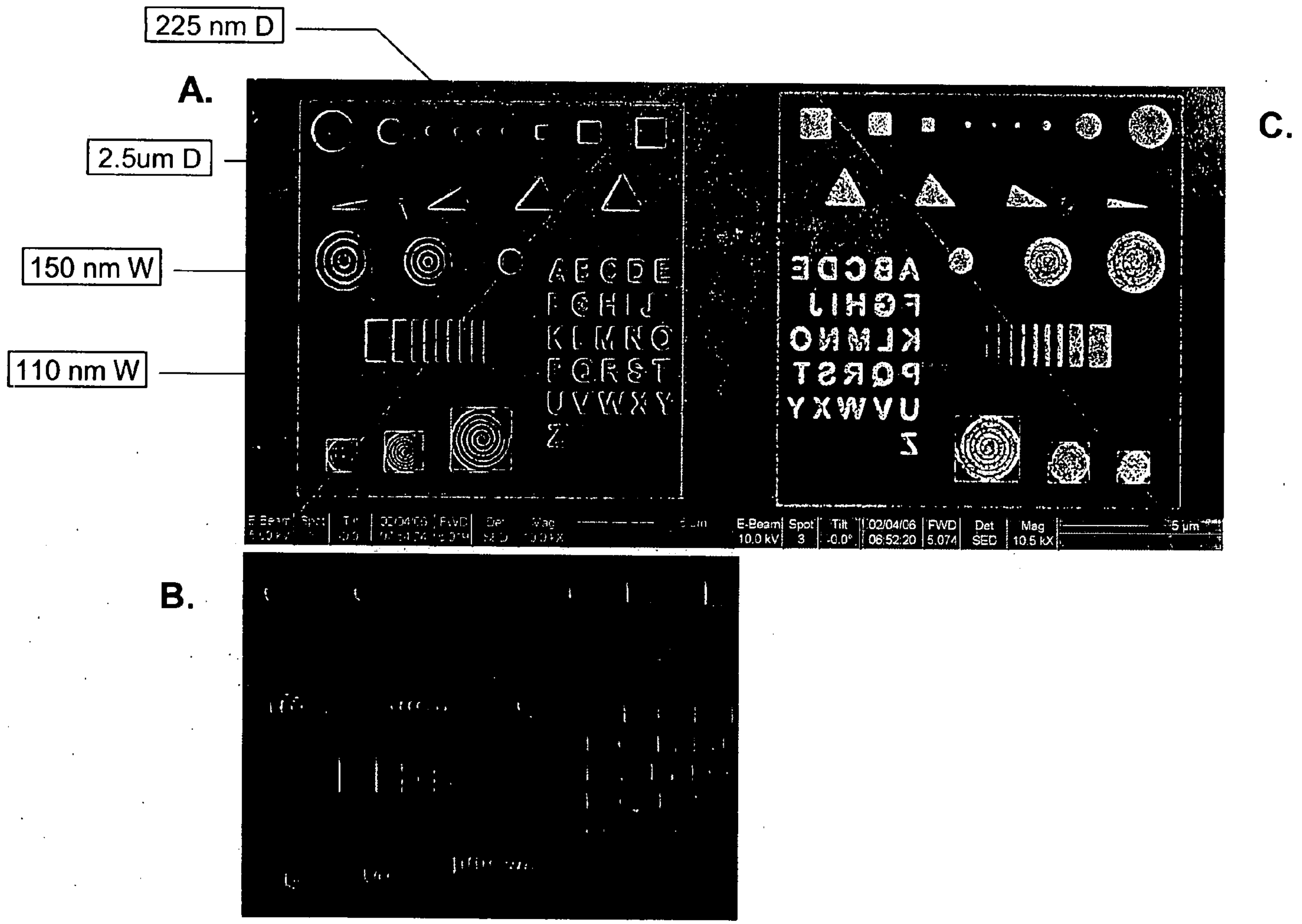

225 nm D
A.
2.5um D
150 nm W
110 nm W
B.
C.
E-Beam 10.0 kV
Spot 3
Tilt -0.0°
02/04/06 06:52:20
FWD 5.074
Det SED
Mag 10.5 kX
5 µm

Fig. 19

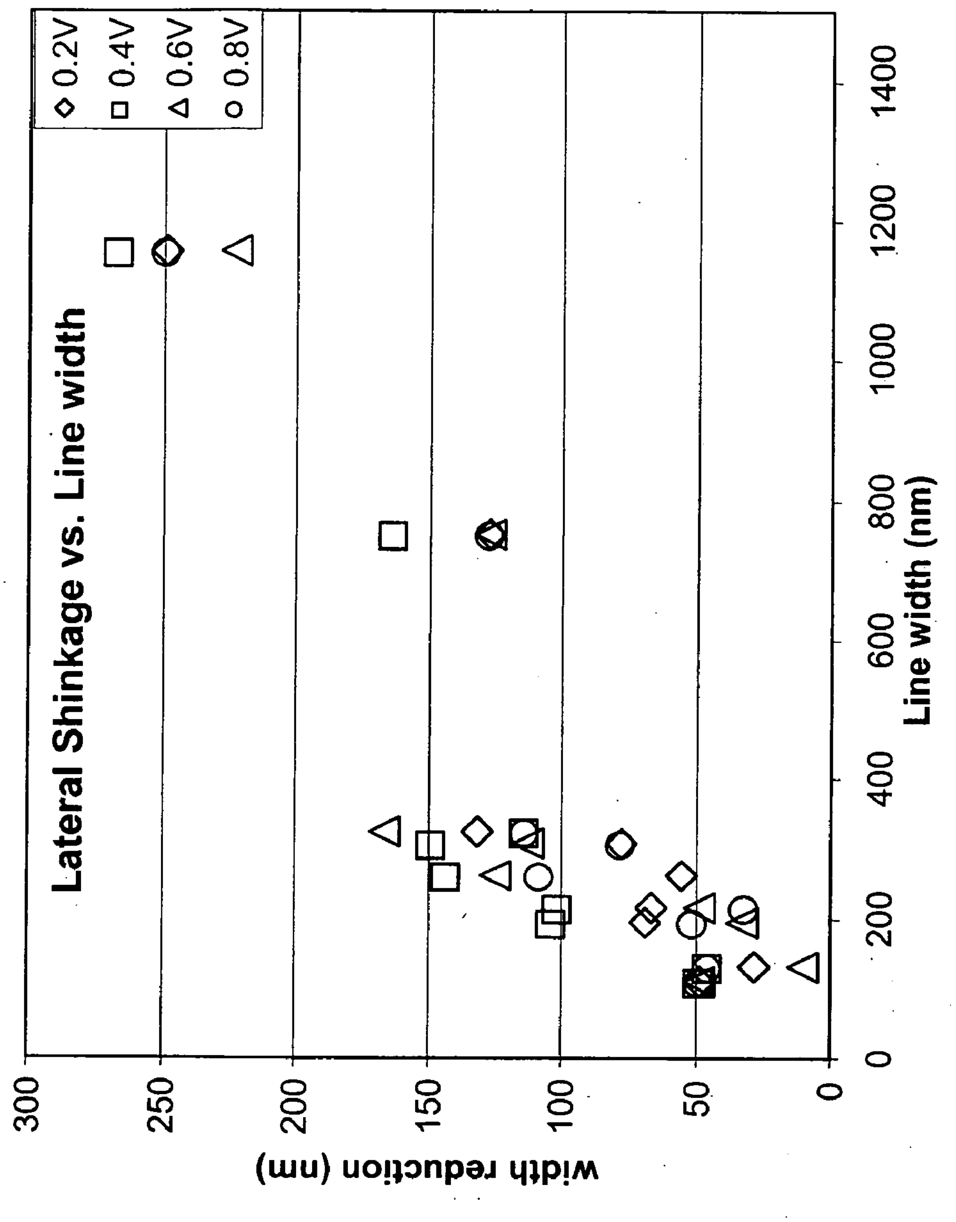

Lateral Shinkage vs. Line width
◇ 0.2V
□ 0.4V
△ 0.6V
○ 0.8V
width reduction (nm)
300
250
200
150
100
50
0
0
200
400
600
800
1000
1200
1400
Line width (nm)

Fig. 20

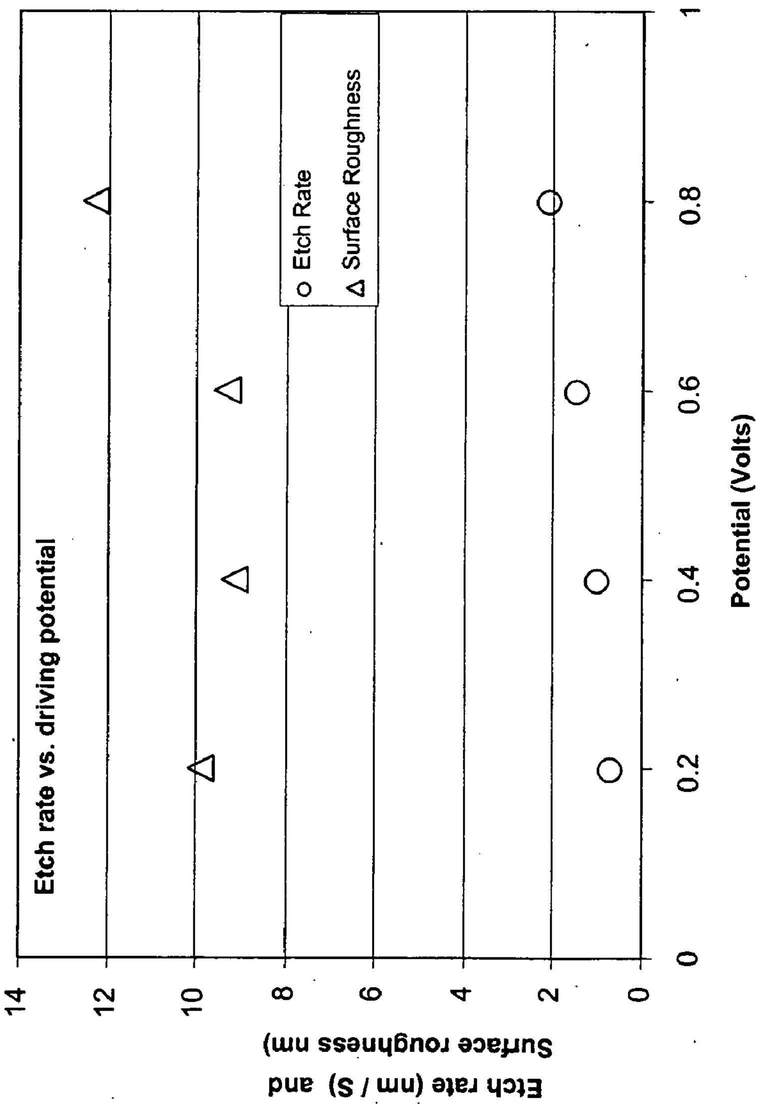

Etch rate vs. driving potential
○ Etch Rate
△ Surface Roughness
Etch rate (nm / S) and Surface roughness nm)
14
12
10
8
6
4
2
0
0
0.2
0.4
0.6
0.8
1
Potential (Volts)

Fig. 21

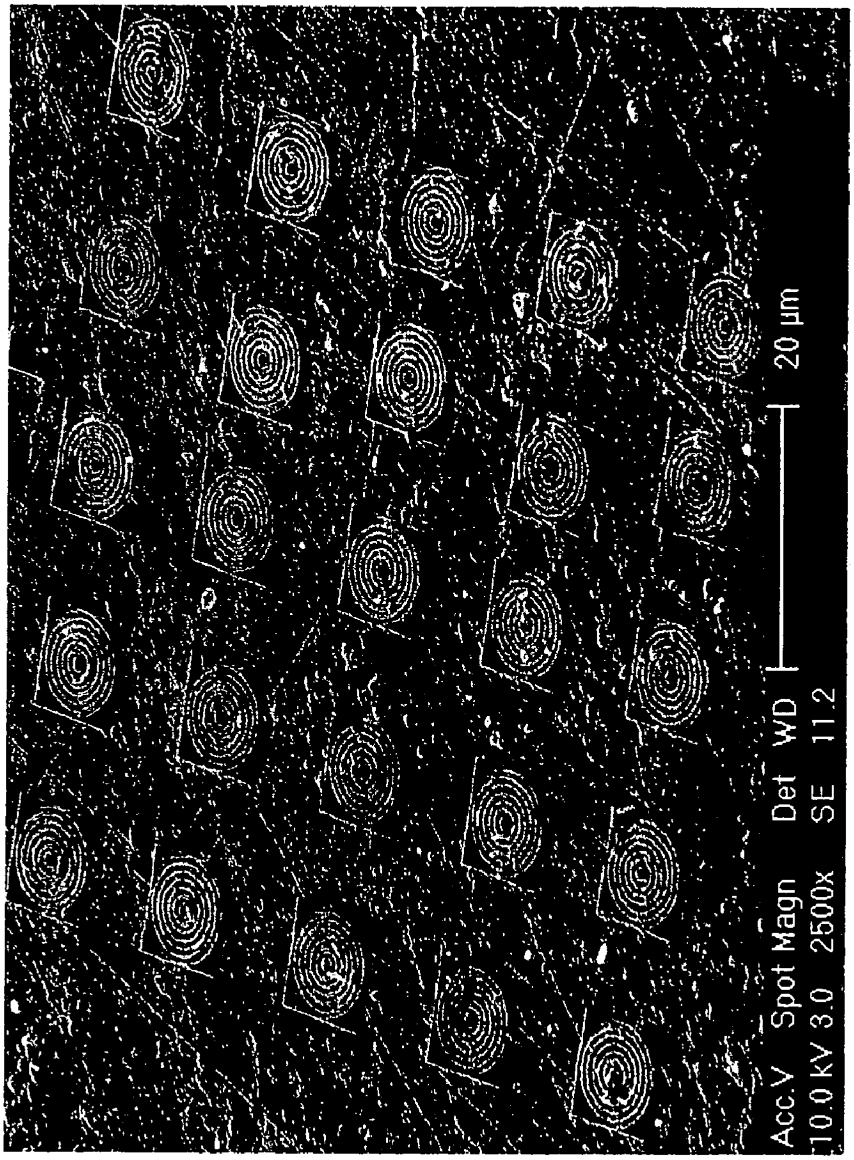


Fig. 22

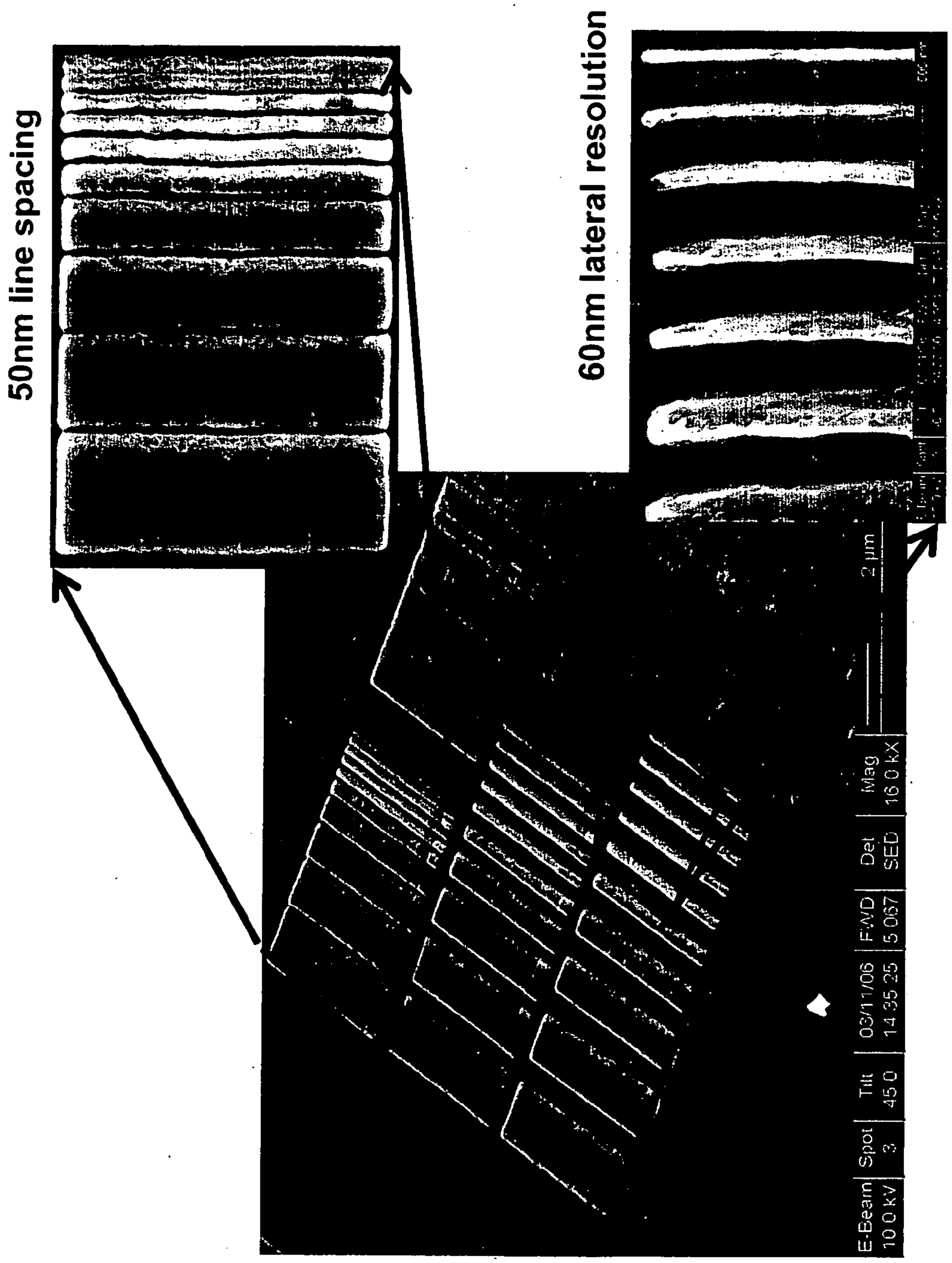

50nm line spacing
60nm lateral resolution
2 µm
E-Beam 10.0 kV
Spot 3
Tilt 45.0
03/11/06 14:35:25
FWD 5.067
Det SED
Mag 16.0 kX

Fig. 23

PATTERN TRANSFER BY SOLID STATE ELECTROCHEMICAL STAMPING

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH OR DEVELOPMENT

[0001] This invention was made, at least in part, with United States governmental support awarded by National Science Foundation under contract number DMI-0328162. The United States government has certain rights in this invention.

CROSS-REFERENCE TO RELATED APPLICATIONS

[0002] Not Applicable.

BACKGROUND OF THE INVENTION

[0003] The use of solid state ionic conductors allows for nano-scale patterning and stamping by highly localized electrochemical etching and deposition. When an electric field is applied by two electrodes in contact with a material that exhibits ionic conduction, the metal ions near one of the electrodes migrate through the bulk of the ionic conductor, and, upon receiving electrons at the counter electrode, reduce back to metal atoms precipitating at the interface. Alternatively, under a reverse potential, a counter electrode of the metal is etched. By nano-patterning the contact between the electrode and the ionic conductor, one can deposit or etch metal patterns at a conductive substrate.

[0004] Electrochemical micromachining, which works by local dissolution of a conducting substrate (metals, semiconductors) under an applied anodic bias in solution, shows promise in fabricating 3D micro and nanoscale structures and devices, since it requires relatively simple equipment and offers rapid etching compared to other techniques such as ion beam milling and laser abrasion. However, a liquid electrolyte, which is difficult to handle, is required as a conducting medium between the two electrodes. This challenge is overcome in the present invention by utilizing solid state ionic conductors.

[0005] Terabe et al, demonstrate the use of mass transport in ionic conductors to implement a quantized atomic conductance switch, QCAS, where the concept of formation and dissolution of nanometer silver cluster was used. In their QCAS, a silver wire with a thin layer of silver sulfide cover was laid on a substrate, and a platinum wire went across it with a gap of one nanometer [K. Terabe, et al., Quantized conductance atomic switch, Nature, Vol 433, 6, Jan. 2005.]. By forming silver cluster from silver ions drawn from underlying silver wire and hence bridging the gap in between, the switch operated at room temperature at a frequency of 1 MHz.

[0006] Terabe et al, show formation and disappearance of nano scale metal cluster on the apex of an Scanning Tunneling Microscopy (STM) tip. Based on the concept of electrochemical reaction, they show growth and shrinkage of a silver pillar of 70 nm in diameter and 200 nm in length on a silver sulfide coated silver STM probe [K. Terabe, et al., Formation and disappearance of a nanoscale silver cluster realized by solid electrochemical reaction, Journal of applied physics, Vol 91, 12, Jun., 2002]. By controlling the current going tunneling through the STM tip and their sample, the growth rate of the silver cluster is regulated.

[0007] M. Lee et al. have used Atomic Force Microscopy (AFM), and a super ionic conductor material, $RbAg_4I_5$, for nanopatterning [M. Lee, et al., Electrochemical nanopatterning of Ag on solid-state ionic conductor $RbAg_4I_5$ using atomic force microscopy, Applied physics letters, Vol 85, 16, Oct. 2004]. With pulsed electric field input through a metal coated AFM probe controlled to step across an $RbAg_4I_5$ sample, they were able to place nanoscale silver cluster with each pulsed bias input, and hence arrange the clusters in designed pattern.

[0008] The use of solid state ionic conduction for switches and for single-point direct writing (with a modified stylus tip) has been previously demonstrated.

[0009] None of these methods, however, are fully adaptable to massive manufacturing due to the slow serial scanning process. Accordingly, there is currently a need in the art for methods of manufacturing structures, including nanostructures, that is capable of high-throughput large area patterning. The invention disclosed herein is a stamping process that can simultaneously produce a number of spatial features and can scale-up to high production rates for massive manufacturing over a large pattern area that conventional approaches cannot match. An additional advantage of the present methods and systems is the ionic stamp can be programmed, scaled and reprogrammed with different metallic nanopatterns for processes such as nano imprint lithography, molding, transfer printing, etc. With appropriate solid electrolytes, the processes disclosed herein can be used to directly produce a structure or desired pattern of structures in different metallic films, substrates, bulk materials or surfaces, thereby saving steps compared to a conventional photolithography patterning process.

SUMMARY OF THE INVENTION

[0010] The present invention provides an electrochemical fabrication platform for making structures, arrays of structures and functional devices having selected nanosized and/or microsized physical dimensions, shapes and spatial orientations. Methods, systems and system components of the present invention use an electrochemical stamping tool for generating patterns of relief and/or recessed features exhibiting excellent reproducibility, pattern fidelity and resolution on surfaces of solid state ionic conductors and in metal layers. Electrochemical stamping tools of the present invention are capable high throughput patterning of large substrate areas and, thus, enable a robust and commercially attractive manufacturing pathway to a range of functional systems and devices including nano- and micro-electromechanical systems, sensors, energy storage devices and integrated electronic circuits. Further, nanopatterning and micropatterning methods and systems of the present invention are compatible with a wide range of materials, including metals, metal alloys, ionic conductors and superionic conductors, and processing conditions, including room temperature (below about 30° C.) processing.

[0011] In one embodiment, the present invention provides methods for making structures, including nanostructures and microstructures, using a stamping tool capable of pattern transfer via electrochemical etching or electrochemical deposition. In a method of the present invention, a first electrode is provided in electrical contact with a solid state ionic conductor. A second electrode is provided in electrical contact with a metal, such as a metal film, substrate, surface, or bulk material, and optionally the metal itself is the second electrode. Electrical contact and/or physical contact is established between at least a portion of the solid state ionic conductor and the metal, for example by a configuration wherein the metal layer is separated from the first electrode by the solid state ionic conductor. In this embodiment of the present invention, the solid state ionic conductor or the first electrode is a stamping tool that generates a pattern of electrical contacts between the stamping tool and the solid state ionic conductor or the metal. Optionally, this method of the present invention may further comprise the step of applying a force to the stamping tool, for example a force that is uniformly applied as a function of a selected area of the stamping tool such that it maintains electrical contact with at least a portion of the stamping tool and the solid state ionic conductor or the metal during processing.

[0012] To generate a structure or pattern of structures, an electric field is established between the first and second electrodes, for example by applying a selected potential difference between first and second electrodes. Application of an electric field results in oxidation of metal atoms in the metal and subsequent migration of ions and electrons generated by the oxidative process. In a useful embodiment wherein the second electrode functions as an anode and the first electrode functions as a cathode, oxidization generates free electrons that migrate toward the electrode having a higher electric potential (i.e. the anode) and mobile metal ions that migrate toward the counter electrode (i.e. the cathode) having a lower electric potential. At the counter electrode (i.e. the cathode) metal ions are reduced back to metal atoms, for example by precipitation at the surface of the counter electrode. The net effect of the oxidation-reduction reactions and ion-electron transport processes is the formation of structures by electrochemical etching of the metal or by electrochemical deposition on a surface of the solid state ionic conductor at the interface with the stamping tool. The present invention, however, also includes patterning methods employing a potential difference wherein the first electrode has a larger electric potential than the second electrode. In this embodiment, oxidation of metal deposits, particles or metals occurs at the first electrode and reduction of metal ions occurs at the second electrode. This aspect of the present invention may be used to dissolve/reactively eliminate metals at the interface between the solid state ionic conductor and the first electrode, in a manner generating a structure or pattern of structures having selected physical dimensions.

[0013] Transport of the metal ions through the solid state ionic conductor is an integral process in the present invention and may involve a transport mechanism involving conduction channels, grain boundaries and/or the presence of bulk defects in the solid state ionic conductor. In one embodiment, a potential difference between first and second electrodes is established and maintained at a value such that oxidation-reduction reactions occur at two interfaces: (i) the interface between the solid state ionic conductor and the metal layer and (ii) first electrode and the solid state ionic conductor. Selection of the appropriate potential difference in this aspect of the present invention depends on the compositions, phases and oxidation-reduction chemistries of the metal layer and solid state ionic conductor, and in some exemplary embodiments range from about 100 mV to about 2000 mV.

[0014] In one embodiment of this aspect of the present invention, a structure or pattern of structures are electrochemically etched into the metal layer using a stamping tool that is the solid state ionic conductor itself. In one embodiment, for example, an ionic conductor-stamping tool is provided having a selected pattern of relief features separated from each other by one or more recessed regions. Patterns of relief features for ionic conductor-stamping tools of the present invention may be generated by any means known in the art including, but not limited to, optical lithograph, electron beam writing, ion beam writing, soft lithograph, wet and dry etching techniques and equivalents known in the art. Physical contact between at least a portion of the relief features and the metal generates the pattern of electrical contacts between the stamping tool and the metal. In this embodiment, applying an electric field results oxidization of metal in regions of the metal in physical contact with at least a portion of the relief features of the stamping tool. Metal ions generated via this oxidative process migrate through the ionic conductor-stamping tool an undergo reduction at the first cathode, thereby resulting in localized electrochemical etching of the metal layer at regions of the metal in physical contact with the relief features of the stamping tool. This embodiment of the present invention provides a means of at least partially transferring a pattern from the stamping tool to the metal layer undergoing processing, for example, by generating the negative relief pattern (i.e. the etch pattern) of at least a portion of the pattern of relief features into the metal layer.

[0015] In another embodiment of this aspect of the present invention, a structure or pattern of structures are electrochemically deposited onto a surface of the solid state ionic conductor using a stamping tool that is the first electrode itself. In one embodiment, for example, a first electrode-stamping tool is provided that has a selected shape that generates a selected pattern of electrical contacts between the first electrode-stamping tool and a surface of the solid state ionic conductor undergoing processing/patterning. Application of an electric field between a first electrode provided at a lower electric potential and a second electrode provided at a higher electrodic potential, results in oxidation of metal atoms of the metal, thereby generating metal ions that migrate to points of electrical contact in the pattern of electrical contacts established between the first electrode-stamping tool and the surface of the solid state ionic conductor. In this method, reduction of metal ions at the interface between the first electrode-stamping tool and the solid state ionic conductor results in localized electrochemical deposition of metal at regions of the solid state ionic conductor in electrical contact with the stamping tool.

[0016] This embodiment of the present invention provides a means of at least partially transferring a pattern from the first electrode-stamping tool to the solid state ionic conductor undergoing processing, for example, by reproducing the relief pattern of at least a portion of the pattern of relief features onto the surface of the solid state ionic conductor in electrical contact with the stamping tool. Useful stamping tools of this aspect of the invention include electrodes, shaped electrodes (e.g. a grid electrode) and electrode arrays. In one embodiment, for example the stamping tool comprises a shaped electrode having plurality of features arranged in a selected pattern, such as a grid electrode, wherein at least a portion of the pattern of the shaped electrode is transferred to a surface of the solid state ionic conductor via localized electrochemical deposition. In another embodiment, the stamping tool comprises an array of electrodes that may be held at substantially the same or, alternatively, different electric potentials (i.e. voltages). In another embodiment a programmable, scalable or reprogramable electrochemical stamping tool is use comprising and array of individually addressable electrodes in electrical contact with the solid state ionic conductor, wherein the voltage on each electrode in the array is independently selectable.

[0017] In methods of the present invention useful for certain applications it is beneficial to use a combination of a metal and solid state ionic conductor comprising metal atoms that having an elemental composition that corresponds to that of the metal used during processing. Use of a combination of elementally matched metal and ionic conductor materials is useful because cations generated from the metal generally will exhibit good transport properties and conductance through the matched solid state ionic conductor in the presence of an electric field, thereby allowing for useful etch rates or deposition rates in the present methods. The present invention includes methods, devices and systems using a combination of a metal and solid state conductor that do not have matched elemental composition with regard to the atomic composition of the metal and the solid state ionic conductor. In these methods and systems, therefore, the composition of the solid state ionic conductor is selected such that it comprises an atom having an elemental composition different from than that of the metal. In these elementally unmatched metal and ionic conductor systems it is useful to choose a metal that generates cations that are capable of efficient transport through the solid state ionic conductor and which exhibit appreciable solubility in the solid state ionic conductor, such that appreciable etching rates and deposition rates may be achieved.

[0018] The present methods are useful for patterning a wide range of metal and solid state ionic materials. Metals and solid state ionic conductors having planar surfaces, contoured (e.g. curved, convex, concaved) surfaces, smooth surfaces, rough surfaces or any combination of these may be patterned using the present methods, devices and systems. The term "metal" is used expansively in the present description and includes bulk metals, metal deposits, metal films, metal substrates, metal particles, aggregates of metal particles, metal clusters, and composite metal materials.

[0019] Another aspect the present invention provides patterning systems using an electrochemical stamping tool capable of electrochemical etching or electrochemical deposition for making a structure or pattern of structures having selected physical dimension, spatial orientation and positions. In one embodiment, a system of the present invention comprises a first electrode in electrical contact with a solid state ionic conductor; and a second electrode in electrical contact with a metal. In this embodiment, the solid state ionic conductor or the first electrode is a stamping tool that generates a pattern of electrical contacts between the stamping tool and the solid state ionic conductor or the metal. Electrical contact and/or physical contact is established between at least a portion of the solid state ionic conductor and the metal, for example by a configuration wherein the metal layer is separated from the first electrode by the solid state ionic conductor. In a useful embodiment, for example, the solid state ionic conductor and the metal are in electrical contact such that generation of an electric field between the first and second electrodes results in oxidation of metal atoms in the metal, thereby generating metal ions and free electrons, wherein the metal ions migrate through the solid state ionic conductor to the first electrode where they are reduced and wherein the free electrons migrate to the second electrode.

[0020] Useful stamping tools for certain embodiments of the present invention have a Young's modulus selected from the range of about 20 GPa to about 200 GPa. A benefit of stamping tools of the present invention having a Young's modulus in this range is that they are less susceptible to pattern distortion than polymeric stamping tools and stamps used in conventional soft lithography patterning techniques, such as conventional nanoimprint lithography. Accordingly, the methods, patterning systems and stamping tools of the present invention are capable of providing good pattern fidelity and high resolution patterning (e.g. resolution less than about 100 nanometers, and more preferably for some applications less than about 50 nanometers). An advantage provided by the present methods, therefore, is the ability to use stamping tools comprising solid state ionic conductor materials having a Young's modulus selected over the range at about 20 GPa to about 200 GPa, which are beneficial for minimizing or completely avoiding stamp distortion during processing.

[0021] In an embodiment providing pattern transfer via electrochemical etching, the ionic conductor is a stamping tool having a selected pattern of relief features, wherein at least a portion the relief features of the stamping tool are provided in physical contact with the metal. This configuration provides a pattern of electrical contacts that is useful for transferring at least a portion of the pattern of the stamping tool (i.e. the relief pattern) to the metal layer via electrochemical etching. Useful stamping tools of this embodiment may have nanosized relief features, microsized relief features or both, for example relief features having nanosized lateral dimensions, nanosized vertical dimensions or both. Use of nanosized and or microsized relief features in this aspect of the present invention beneficial for establishing electrical contact limited to selected nanosized and/or microsized regions of the surface of the solid state ionic conductor undergoing processing. This stamping tool configuration is useful for generating nanosized and/or microsized structures and patterns of nanosized and/or microsized structures

[0022] In an embodiment providing pattern transfer via electrochemical deposition, the first electrode is a stamping tool comprising a shaped electrode having a plurality of structural features, such as a grid electrode, or an array of electrodes provided in electrical contact with the solid state ionic conductor. Electrode and electrode array geometries having nanosized or microsized elements is beneficial for establishing electrical contact limited to selected nanosized and/or microsized regions of the surface of the solid state ionic conductor. This stamping tool configuration is useful for generating nanosized and/or microsized structures and patterns of nanosized and/or microsized structures. Embodiments of this aspect of the present invention also includes use of a scalable, programmable and/or reprogrammable stamping tool comprising an array of individually addressable electrodes, wherein the voltage on each electrode in the array is independently selectable. Use of stamping tools comprising individually addressable electrodes is useful for making a wide range of structures, patterns and devices as the rate and extent of electrochemical deposition on the solid state ionic conductor surface can be individually and separately adjusted for each electrode in the array, thereby providing a fabrication pathway to structures and patterns of structures having a range of physical dimensions.

[0023] An embodiment of the present invention is a method of etching a metal layer. The method for making a structure comprises providing a first electrode in electrical contact with a metal and in electrical contact with a solid state ionic conductor, wherein said metal surface covers at least a portion of a surface of said solid state ionic conductor; providing a second electrode electrically connected to a conductive material, including a metal, metal surface, metal layer or bulk metal; establishing electrical contact between at least a portion of said solid state ionic conductor and said conductive material; and generating an electric field between said first and second electrodes, wherein metal atoms in said metal are oxidized, thereby generating metal ions and free electrons, wherein said metal ions migrate through said solid state ionic conductor to said second electrode where they are reduced and wherein said free electrons migrate to said first electrode, thereby making said structures. In an embodiment, the metal located on a solid state ionic conductor is formed by one of the processed disclosed herein.

[0024] The method can further comprise the first electrode that is an anode and the second electrode that is a cathode.

[0025] In an embodiment, the electrical contact between said first electrode and said metal is a single point contact. In an embodiment, the electrical contact between said first electrode and said metal is an electrical contact pattern. In an embodiment the electrical contact pattern is generated by a stamping tool. In a further embodiment, the electrical contact pattern is generated by the first electrode having a plurality of features arranged in a selected pattern, and wherein at least a portion of the pattern is transferred to a surface of said metal via localized electrochemical etching. In an embodiment, the metal surface is the top surface of a metal layer having a depth or a thickness that ranges between a few nanometers to bulk

[0026] The composition, physical state, and physical dimensions of metal layers and/or solid ionic conductors of the present invention are important parameters in patterning methods and systems of the present invention. In a useful embodiment, the metal layer has a thickness selected from the range of about a few nanometers to bulk dimensions (e.g. greater than 1 micron), and the solid state ion conductor has a thickness selected from the range of about 100 nanometers to about bulk dimensions (e.g. centimeters). Useful solid state conductors have an ionic conductivity selected from the range of about 0.001 S/cm to about 500 S/cm and include, but are not limited to, Ag_2S, Cu_2S, AgI, $RbAg_4I_5$, Ag_3SI, AgCuS, AgCuSe, and $Br_4Cu_{16}I_7Cl_{13}$, composite materials, materials that are amorphous solids, semicrystalline solids or single crystalline solids. In some embodiments of the present invention providing large etch rates or deposition rates, a solid state ionic conductor is used having a relatively large ionic conductivity, and in some embodiments of the present invention providing small etch rates or deposition rates, a solid state ionic conductor is used having a relatively small ionic conductivity. The present methods and systems include use of solid state ion conductors that are superionic conductors. Useful metals for the methods and systems of the present invention include, but are not limited to, Ag, Cu, Au, Pb, Zn, and other materials that are conductive. In an embodiment, the metal composition matches the metal composition of the solid state ionic conductor.

[0027] In another aspect, the present invention provides an electrochemical stamping tools for etching structures into a metal comprising: (i) a first electrode having a first electric potential; (ii) an ionic conductor having a selected pattern of relief features, wherein the ionic conductor is in electrical contact with the first electrode and wherein at least a portion of the relief features are capable of establishing electrical contact with the metal; and (iii) a second electrode having a second electric potential that is higher than the first electrode.

[0028] In another aspect, the present invention provides an electrochemical stamping tool for generating structures on a solid state ionic conductor comprising: (i) a first electrode having a first electric potential; (ii) an ionic conductor having a selected pattern of relief features, wherein the ionic conductor is in electrical contact with the first electrode and wherein at least a portion of the relief features are capable of establishing electrical contact with a metal; and (iii) a second electrode having a second electric potential that is higher than the first electrode, wherein the second electrode is in electrical contact with the metal or is the metal itself.

[0029] In another aspect, the present invention provides an electrochemical stamping tool for generating structures on a solid state ionic conductor comprising: (i) a first electrode comprising a plurality of features arranged in a selected pattern, wherein at least a portion of the features are capable of establishing electrical contact with the solid state ionic conductor; and (ii) a metal in electrical contact with solid state ionic conductor. Optional, an electrochemical stamping tool of this aspect of the present invention further comprises an electrode array, wherein electrodes in the array are in electrical contact with the solid state ionic conductor undergoing processing/patterning.

[0030] In another aspect, the present invention provides a method of making a structure comprising the steps of: (i) providing a first electrode in electrical contact with a solid state ionic conductor; (ii) providing a second electrode in electrical contact with a metal; (iii) establishing electrical contact between at least a portion of the solid state ionic conductor and the metal; and (iv) generating an electric field between the first and second electrodes, wherein metal in the metal is oxidized thereby generating metal ions and free electrons, wherein the metal ions migrate through the solid state ionic conductor to the first electrode where they are reduced and wherein the free electrons migrate to the second electrode, thereby making the structures; wherein the solid state ionic conductor or the first electrode is a stamping tool that generates a pattern of electrical contacts between the stamping tool and the solid state ionic conductor or the metal.

BRIEF DESCRIPTION OF THE DRAWINGS

[0031] FIG. **1** provides a schematic diagram illustrating a general system without electric potential (FIG. **1***a*), a deposition system (FIGS. **1***b-d*), an etching system (FIG. **1***e*), and an electrochemical patterning system (FIG. **1***f*) for generating nanostructures. In this embodiment, the solid state ionic conductor is Ag_2S, the metal is silver, and the anode and cathode are connected to a power supply with reversible polarity so that the location of the anode and cathode change from the bottom and top, respectively (FIGS. **1***b-d*) to the top and bottom (FIG. **1***e*). FIGS. **1***b-d* illustrate building of nanostructures by deposition. FIG. **1***e* illustrates reversing the electric potential builds nanostructures by etching metal overlaying the solid state ionic conductor. The direction of the current is indicated by the arrows showing the flow of electrons ("e^-").

[0032] FIG. **2** provides atomic force microscopy (AFM) micrographs illustrating the writing and dissolution of silver structures using the scheme depicted in FIGS. **1***b-e* using an AFM electrode. FIG. **2** comprises five frames: frame **1** is an AFM photograph the surface of the Ag_2S before the process; frames **2**-**5** are AFM images of the surface after each line in the asterisk is drawn.

[0033] FIG. **3** provides atomic force microscopy (AFM) photographs (FIGS. **3**A & C) and corresponding height measurements (FIGS. **3**B & D) illustrating the dissolution and growth of silver structures. The lines in A and C track the positions at which heights are measured in B and D. The silver clusters are written to a height of about 250 nm (see B and D) and dissolved to a height of about 150 nm (see A and C).

[0034] FIG. **4** shows AFM images of electrochemical stamping of silver structures on Ag_2S with a stamping tip using the scheme shown in FIG. **1***f*. The top panel (A) shows the Ag_2S surface prior to stamping, the middle panel (B) shows one stamped nanostructure (see structure within the highlighted circle), and the bottom panel (C) three replicated nanostructures.

[0035] FIG. **5** shows optical images of large-area electrochemical stamping with micrometer resolution. The top panel (A) shows the silver sulfide stamping tool and the bottom panel (B) shows the etched silver film. The bar is 200 μm.

[0036] FIG. **6** is a photograph of a system for electrochemical stamping. Positioning stages are labeled (a) and (b). Electrodes are labeled (c) and (e). Optical microscopy for process monitoring is labeled (d).

[0037] FIG. **7** is a time-lapsed sequenced of optical microscope image of solid-state electrochemical stamping as produced by the system of FIG. **6** using a silver sulfide stamping tool on a Ag surface on chrome on glass. A is prior to stamping; B is an intermediate stage; and C is when stamping is substantially complete.

[0038] FIG. **8** is a cyclic voltammetry characterization of a silver sulfide stamping tool to determine typical redox potential of Ag/Ag^+. The black lines are ramping up and the red lines are ramping down, as indicated in the legend.

[0039] FIG. **9** provides a series of current as a function of time for metal etching with a silver sulfide stamping tool for four different voltages as indicated.

[0040] FIG. **10**A provides an AFM image of three Ag clusters Ag clusters (identified by number 1, 2 and 3 in the bottom panel) drawn to the surface of a Ag_2S film by means of a charged AFM tip. The three clusters have similar topography. The top panel is the surface of the Ag_2S film before and the bottom panel after application of an electric potential. The bar is 1 μm. FIG. **10**B provides a schematic illustration of a transfer stamping process, where a programmable Ag_2S stamping tool (panel a) is brought into contact with Ag film surface and a potential difference between the cathode and anode applied (panel b) to selectively etch Ag substrate or Ag film to provide a three-dimensional profile on the surface (panel c).

[0041] FIG. **11** provides experimental characterization of superionic conduction at nanoscale. FIG. **11**A provides a graphical representation of cyclic voltammetry to monitor the stamp etching process conditions. FIG. **11**B is an SEM image of a cross-section of the Ag_2S stamping tool, revealing directional formation of silver nanowires at a scale <100 nm.

[0042] FIG. **12** provides an overview of a stamping process. FIG. **12**A is a schematic showing a cathode-anode pair, with an Ag_2S shaped stamping tool in electrical contact with, and positioned between, the cathode and Ag film. FIG. **12**B is an SEM image of an Ag_2S stamping tool prepared by Focused Ion Beam (FIB) milling (scale bar 5 um). FIG. **12**C is an SEM image of a sub-micron line etched out of an Ag metal (scale bar 5 um).

[0043] FIG. **13** provides a schematic for a self-sustaining nano-ionic system that use patterns made by the methods disclosed herein.

[0044] FIG. **14** provides a schematic of an electronically reconfigurable plasmonic switch using growth and dissolution of Ag nanodots. When the polarity of the switch reversed (compare FIGS. **14**A and **14**B), the optical lightwaves are guided to the corresponding branches, as the overgrowth of nanodots experience a red-shift in wavelength and reject the light signal. The top panel of each of A and B are side views, and the bottom panels are top views.

[0045] FIG. **15**A is an SEM image of a Ag_2S stamping tool of the present invention. FIG. **15**B is an SEM image of the corresponding Ag film electrochemically stamped by the stamping tool of FIG. **15**B. The scale bar is 1 um.

[0046] FIG. **16** provides a schematic illustration of etching a metal with an electrochemical stamp or stamping tool. FIG. **16**A shows a metal (Ag) and a solid state ionic conductor (Ag_2S) having a three-dimensional surface (e.g. the stamp) that are not in electrical or physical contact. FIG. **16**B shows the stamping process, wherein only a portion of the stamp surface and metal are in electrical contact. There is a detailed view of the boxed region showing that where the Ag_2S and Ag are in contact, oxidation of metal on the metal surface occurs, but substantially no oxidation occurs on the metal surface that is not in contact with the Ag_2S conductor. After the stamping process is complete, the stamp is removed from the metal leaving a three-dimensional pattern in the surface of the metal, as shown in FIG. **16**C.

[0047] FIG. **17** provides cyclic voltametry plots of the silver sulfide stamp measured between two silver electrodes.

[0048] FIG. **18** provides plots of current as a function of time for various driving potentials during an etching process.

[0049] FIG. **19** is a pair of SEM images showing a silver sulfide stamp (A top view; B perspective view) and the corresponding produced silver feature (C) etched from a silver film.

[0050] FIG. **20** is a plot of lateral width reduction as a function of line width for four driving potentials indicating that for the smallest line width stamp (110 nm), a driving potential of 0.6V provides the lowest lateral width reduction so that the feature is reduced by 13% (e.g. 95 nm width).

[0051] FIG. **21** is a plot of etch rate (nm/s) and surface roughness (nm) as a function of the driving potential (volts).

[0052] FIG. **22** is an SEM photograph of an etched silver metal made with an electrochemical Ag_2S stamping tool patterned with a 5×5 plasmonic array.

[0053] FIG. **23** provides SEM images showing the resolution of patterns etched into silver metal using an Ag_2S electrochemical stamping tool of the present invention. Two regions of the etched surface are expanded to show the invention provides for pattern creation with line spacing of 50 nm and lower and lateral resolution of 60 nm and better.

DETAILED DESCRIPTION OF THE INVENTION

[0054] The invention may be further understood by the following non-limiting examples. All references cited herein are hereby incorporated by reference to the extent not inconsistent with the disclosure herewith. Although the description herein contains many specificities, these should not be construed as limiting the scope of the invention but as merely providing illustrations of some of the presently preferred embodiments of the invention. For example, thus the scope of the invention should be determined by the appended claims and their equivalents, rather than by the examples given.

[0055] As used herein, "structure" is used broadly to refer to formation of patterns, including recessed, relief, or a combination of recessed and relief patterns. A recessed pattern refers to a pattern that is formed by etching a surface, such that channels and/or depressions are formed on the surface. This is also commonly known as "top-down" manufacture. A relief pattern is one that is formed by deposition of material onto a surface to form a pattern. This is also commonly known as "bottom-up" manufacture. The structure can be a three-dimensional pattern, having a pattern on a surface with a depth and/or height to the pattern. Accordingly, the term structure encompasses geometrical features including, but not limited to, any two-dimensional pattern or shape (circle, triangle, rectangle, square), three-dimensional volume (any two-dimensional pattern or shape having a height/depth), as well as systems of interconnected etched "channels" or deposited "walls." In an embodiment, the structures formed are "nanostructures." As used herein, "nanostructures" refer to structures having at least one dimension that is on the order of nanometers to microns. In an embodiment the nanostructure has at least one feature that is on the order of tens of nm. For example, the width of the line can be on the order of 10's to 100's of nm and the length can be on the order of microns to 1000's of microns. In an embodiment the nanostructure has one or more features that range from an order of tens of nm to hundreds of nm.

[0056] A "pattern of structures" refers to a plurality of structures that are deposited and/or etched on a surface by a stamp or stamping tool. Accordingly, the term encompasses a plurality of geometrical features etched onto a surface, as well as a plurality of geometrical features deposited onto a surface. The present methods and system are capable of generating patterns of structures having well defined and selected physical dimensions, spatial orientations and positions.

[0057] A "stamp" or a "stamping tool" refers to a material having a surface that is shaped for etching and/or depositing a pattern of structures. Accordingly, the stamping tool can have one or more recessed features and/or one or more relief features that define the stamp's "shaped surface." The stamping tool facilitates pattern transfer from the stamp surface. The stamp's "shaped surface" is a three-dimensional shape on the surface that makes electrical contact with a metal surface and, in particular, an electrical contact that is a "pattern of electrical contacts." In an embodiment, the composition of the stamping tool comprises a solid-state ionic conductor. In an embodiment, the stamping tool comprises one or more features on an electrode. A feature on an electrode is a shape that provides an electrical contact pattern. Depending on the process, and in particular the direction of the electric field (e.g. relative electric potentials of the electrodes), the stamping tool can deposit metal structures on a substrate surface to make a relief pattern of structures, or the stamping tool can etch a metal surface to make a recess pattern of structures that correspond to the stamp relief features. In an embodiment, the generated structure comprises both a relief structure and a recess structure. The stamping tool relief features can be constructed by methods known in the art, including by focused ion beam milling. The surface of the stamp that makes electrical contact with a conducting surface can have any shape, including substantially planar, curved, or a combination of planar and curved,

[0058] The dimensions of the relief feature can be microsized, nanosized, or both microsized and nanosized. A feature is microsized if it has dimensions on the order of greater than microns. A feature is nanosized if it has any one or more dimensions on the order of less than about one micron. In an embodiment, a nanosized feature is less than about 100 nm. A "lateral dimension" refers to a distance that is parallel to the interaction surface of the stamping tool and solid ionic conductor or the stamping tool and the metal. A "vertical dimension" refers to the height of the relief feature.

[0059] "Electrical contact" refers to the configuration of two or more elements such that a charged element is capable of migrating from one element to another. For example, a cathode in electrical contact with a solid state ionic conductor permits a metal ion to migrate from the interior of the solid state ionic conductor to the region between the surface of the cathode and the surface of the conductor, where the metal ion is reduced. Similarly, an anode in electrical contact with a metal permits free electrons released due to metal atom oxidization to flow from the metal to the anode. Accordingly, electrical contact encompasses elements that are in "physical contact." Elements are in physical contact when they are observable as touching. Electrical contact also includes elements that may not be in direct physical contact, but instead may instead have an intervening element, such as an electrolyte or a conductive material, located between the two or more elements. Accordingly, electrical contact encompasses an electrode and a solid state ionic conductor, wherein metal is deposited and reduced between the surface of the electrode and the solid ionic conductor.

[0060] "Pattern of electrical contacts" refers to a pair of surfaces that have regions of electrical contact and regions of no electrical contact. For example, in the processes disclosed herein, a stamping tool of the present invention is said to have a "pattern of electrical contacts" with a metal so as to generate an etched structure. In an embodiment, the pattern of electrical contacts corresponds to a pattern of physical contact between the stamping tool and the surface to be etched. In an embodiment, the pattern of electrical contacts corresponds to a pattern of physical contact between the stamping tool and the substrate surface on which the deposited metal rests. The process of reducing ionized metal atoms at the interface between the stamp and solid state ionic conductor is referred to as "electrochemical deposition." The process of oxidizing metal at the physical contact pattern between the stamping tool and the metal surface is referred herein as "electrochemical etching." Accordingly, the stamp or stamping tool is also referred herein as an "electrochemical stamp," wherein the stamping tool can be used to etch or deposit metal.

[0061] "Localized electrical deposition" refers to deposition that is substantially restricted to an area defined by a region between the stamping tool and the solid state ionic conductor. Outside this region, substantially no reduction of ions, and corresponding deposition, occur. In an embodiment, substantially no reduction refers to a region outside the physical contact area between the stamping tool and metal or stamping tool and solid state ionic conductor.

[0062] The stamp and/or the stamping tool has mechanical attributes and characteristics, including Young's modulus, compressibility modulus, conductivity, flexural rigidity, that are optimized as known in the art to ensure suitable structures are obtained from any of the processes disclosed herein. In an embodiment, a separate element such as a rubber or other elastomeric material, is incorporated into a stamping tool to ensure that as the deposition and/or etching process proceeds, physical contact is maintained between the stamp and surface during etching and/or deposition. In an embodiment, a force actuator is connected to the stamping tool for applying a constant and uniform force, and corresponding pressure, between the stamping tool and solid state ionic conductor or metal throughout processing. A force is said to be uniformly applied to a surface such that the pressure distribution between the stamping surface and metal is substantially uniform, thereby ensuring the stamping tool remains level relative to the metal. In other words, the etch rate is uniform over the metal surface, and is independent of location on the metal surface. In addition, a uniform force ensures continued physical contact between the stamping tool and the etched metal throughout the etching process.

[0063] "Cathode" and "anode" have their art-recognized meanings. An anode is an electrode where oxidation occurs and a cathode is where reduction occurs. An anode and cathode form an electrode pair where, when each are charged to different electric potentials and used in a process disclosed herein, redox reactions occur. The cathode and anode are made from materials known in the art. In an embodiment the cathode and anode are platinum. The electrodes are each electrically connected to a power supply, so that electrons generated at the anode travel to the cathode.

[0064] A "solid state ionic conductor" refers to a material that is in a solid-state and can conduct ions. The solid state ionic conductor functions as a membrane that separates the anode from the cathode, such that at least a portion of the oxidized metal travels from the anode, through the solid ionic conductor, to the cathode surface. Preferred solid state ionic conductors have the property of being fast and selective conductors of a metal ion. The solid state ionic conductor has an ionic conductivity so that patterned structures are obtained. For example, the ionic conductivity can be between about 0.001 to 500 S/cm^2, wherein the ionic conductivity is selected so as to obtain a desired etch rate. The solid state ionic conductor includes any materials that are solid-state and selectively conduct metal ions. For example, the solid state ionic conductor encompasses materials that are amorphous solids, have grain boundaries, electroactive polymers, composites and/or comprise single crystalline materials. Polymers and glasses can also comprise solid state ionic conductor. The solid state ionic conductor can comprise a composite material having a mobile ionic conductive phase embedded in a host matrix. Useful solid state ionic conductors of the present invention include a mobile ionic conductive phase in a polymer or glass host matrix and include nano particle composite materials. The solid electrolyte can comprise those disclosed in U.S. Pat. Pub. No. 2003/0044687 (a first binding polymer and a second polymer composed of alkali metal ion conducting polymers), U.S. Pat. No. 6,165,705 (MAg_4I_5, where M is a monovalent cation), and others known in the art, including but not limited to, Ag_2S, AgI, $RbAg_4I_5$, Ag_3SI, AgCuS, AgCuSe, $Br_4Cu_{16}I_7Cl_3$, and Cu_2S.

[0065] "Potential difference" refers to a cathode and anode having different electric potentials to generate an electric field, such that electrons migrate to the anode, and ions selectively migrate from the anode to the cathode via a path through the solid state ionic conductor positioned between the anode and cathode.

[0066] "Metal,""Metal film" or "metal layer" refers to a metal material having a surface where oxidation and/or reduction may occur. In an embodiment, the metal is an integral part of the electrode such that the metal is at least a portion of the electrode. In an embodiment, the metal is a metal surface of a metal film, bulk metal, metal substrate, metal particle, metal cluster, metal composite or metal layer that is electrically connected to the electrode. In an embodiment, the metal is a bulk metal. "Bulk metal" refers to a metal that is shaped so that it has dimensions on the order of microns and higher. A dimension referred to as "bulk" has a length on the order of microns and higher. In an embodiment the metal is adjacent and covers at least a portion of a substrate. In an embodiment, the substrate provides structural support to a metal and assists in positioning the metal relative to the counter electrode or the stamping tool. In an embodiment, the substrate comprises chrome or glass. In an embodiment, the substrate comprises a translucent material, or a window, to assist in optical visualization of the process. In an embodiment, the substrate is a solid state ionic conductor. In an embodiment, the thickness of the metal layer is between about 10 nm and 5 mm. In an embodiment, the thickness of the metal layer is between 10 nm and 1 μm. In an embodiment, the thickness of the metal layer is between 10 nm and 500 nm. In an embodiment, the thickness of the metal layer is about 200 nm. In an embodiment the metal layer comprises Ag, Au, or Cu. In an embodiment, the metal layer is Ag.

[0067] A metal ion is said to "migrate through" the solid ionic conductor under an electric potential when the metal ion travels from the surface of the metal in electrical contact with the anode to the surface of the cathode by a path within the solid ionic conductor.

[0068] An "individually addressable electrode" refers to an electrode that comprises an array of electrodes, wherein each member of the array is independently controllable. Independently controllable refers to an electrode having a potential that can be varied independently of the potential of other electrode array members. An individually addressable electrode is accordingly reprogrammable and reconfigurable, such that a single stamp or stamping tool can be used to generate different structures, and provide a user more control over generated structures. Individually addressable electrodes permit pattern transfer that is programmable and/or scalable. A programmable, reprogrammable and/or scalable electrode array permits a single stamping tool to be variable configurable such that a single stamp can create any number of patterns by electronically controlling the electric potential distribution across the surface of the stamp. A programmable, reprogrammable and/or scalable electrode array is capable of generating different, independently selectable patterns on surface or in materials using the same stamping tool.

[0069] A stamping tool is said to have features of "substantially the same voltages" when there is less than about 5% voltage variation between features, including less than about 1% voltage variation between features. A stamp having features of "substantially different voltages" refers to a voltage variation of any one or more feature being greater than 1%, including greater than 5%.

[0070] In the following description, numerous specific details of the devices, device components and methods of the present invention are set forth in order to provide a thorough explanation of the precise nature of the invention. It will be apparent, however, to those of skill in the art that the invention can be practiced without these specific details.

[0071] This invention provides methods for making patterns, including micropatterns, nanopatterns and a combination of micro and nanopatterns. The present invention provides methods of patterning by electrochemical stamping, to provide relief and/or recess features directly to a metal surface or metal overlaying a substrate surface, wherein the substrate surface is a solid state ionic conductor.

[0072] FIG. **1** provides a schematic diagram illustrating a side view of a pair of electrodes, between which lie a solid state ionic conductor (e.g. Ag_2S) and a metal (e.g. Ag). A distinct property of solid-state ionic conductors is that an electric field can induce ion migration resulting in mass transport, providing the mechanism of electrochemical deposition and etching, including structures having nanoscale to microscale dimensions. Some examples of solid-state ionic conductors are copper sulfide (Cu_2S), silver iodide (AgI), silver sulfide (Ag_2S), etc. FIG. **1** shows the basic schemes for electrochemical patterning. A silver film **20** (connected to one electrode **30**) is separated from the counter electrode **30** by a solid electrolyte **10**, silver sulfide for example. Under an electric field generated by a power supply **35** (see FIG. **1**(*b*)), silver atoms at the silver substrate **20** are oxidized into silver ions **42** and electrons **44**. While electrons move to the anode electrode **40** and then the cathode electrode having higher potential **50**, mobile silver ions **42** migrate through the conduction channels formed by the accumulation of defects in the ionic conductor bulk **10** to the counter electrode **50** where, with the available electrons, they are reduced back to silver atoms **60** (see FIG. **1**(*c*)) to form a metallic nanostructure. This is depicted in FIGS. **1** (*b*)-(*d*). The bias between sample **20** and electrode **50** is such that the redox reaction takes place at two interfaces, one between silver sulfide **10** and the underlying silver film **20**, the other between electrode **50** and silver sulfide substrate **10**.

[0073] FIGS. **1** (*d*)-(f) depict producing metallic nanostructures by a writing tool **68**. FIG. **1**(*d*) shows the writing feature of a sharp tip electrode **68** that deposits Ag **60** on an Ag_2S substrate surface **10**. FIG. **1**(*e*) shows the erasing feature of a sharp tip electrode by moving the sharp tip electrode under a reverse electric field such that the cathode **50** and anode **40** reverse relative to writing scheme depicted in FIGS. **1**(*b*)-(*d*), such that a portion of the metal layer **60** is erased. FIG. **1**(*f*) illustrates the use of a stamp **70** connected to a cathode **50** for single-step production of a patterned deposited structure **60** on the surface of the solid state ionic conductor **10**.

[0074] FIGS. **2** and **3** show AFM images of the results obtained using the process summarized in FIG. **1**. FIG. **2** demonstrates use of the process to write a silver asterisk by a sequence of lines as shown. Panel **2** contains a single silver line, panel **3** contains two lines forming an X shape, Panels **4** and **5** show the three lines forming an asterisk. FIG. **3** shows the growth and dissolution of a silver pillar by reversing the electric field. The silver structure was grown to 250 nm (FIGS. **3**C and **3**D) and then dissolved to 150 nm (FIGS. **3**A and **3**B).

[0075] FIG. **4** shows the results for a process using silver metal and a silver sulfide solid state ionic conductor. A silver microstructure is circled in FIG. **4**B. Additional silver microstructures are drawn out of the silver sulfide sample by a charged AFM tip, with three such structures shown in FIG. 4C.

[0076] Stamping experiments implement the concept depicted in FIG. **1**(*f*), wherein an electrode with a desired pattern is brought into contact with a metal surface. With an electric field generated between the anode and the cathode and across the solid ionic conductor, repeated metal structures are drawn out of the ionic conductor and deposited on its surface. In an alternate embodiment, a pre-patterned solid state ionic conductor stamp is placed in physical contact with a metal, and electrical potential with the correct polarity applied (e.g. silver having a higher potential than the anode that is connected to the stamp). Under this electrical potential, the metal atoms on the substrate in immediate contact with the stamp are ionized into mobile metal ions that migrate into the stamp and free electrons that move through the remaining metal to the anode. Accordingly, only the portions of the metal in contact with the stamp are etched. The etching process proceeds until substantially all the metal atoms making up the film are oxidized and absorbed into the stamp, revealing an optional underlying chrome film or the process is ended by terminating the applied electric field. Any connection, so long as continued conductivity is maintained during the process, is encompassed by the present invention.

[0077] FIG. **5** is an optical microscopy image of one such patterning process. FIG. **5**A shows the pattern of the silver sulfide stamp. FIG. **5**B is the corresponding pattern etched into the surface of a silver film. The stamp is cut out of a silver sulfide crystal and pressed between two flat parallel surfaces to maximize the contact between the silver film and the stamp. The stamp is pre-patterned with a grating pattern on one side, and secured to a platinum electrode on the other, and mounted on a column. The patterned face of the stamp is brought in contact with a glass substrate having a 100 nm layer of silver deposited over a layer of chrome using a mild pressure and corresponding force. An elastomer material (see element **75** in FIG. **12**A) is optionally inserted between the column and the electrode and initially compressed by the pressure between the stamp and the contact. This elastomeric material serves as a compliant mechanism that gradually relaxes to maintain good contact between the stamp and the substrate as the silver layer is etched during the electrochemical process. Application of a constant force or pressure ensures steady contact is maintained between the stamp and the metal thereby maximizing the resolution and repeatability of generated structures. Suitable elastomeric materials including, for example, rubber, are commercially available. Commercially available polymer-based visco-elastic material include, for example, Sorbothane®, and PDMS or other silicone rubbers. In an embodiment, the force actuator comprises an compressible elastomeric material.

[0078] FIG. **6** shows a system used for an etching procedure. An optical microscope is placed underneath the glass sample stage to image the bottom surface of the glass sample. The entire etching process is monitored by observing the color change of the contact area between the film and the stamp due to the change of the thickness of the silver film. Electric current and time are also monitored and synchronized with the digital video captured through the microscope. This combination of quantitative (current and time) and qualitative data acquisition (video image, color monitoring) allows visual events to be matched with current changes, thereby permitting a more in-depth analysis of the electrochemical process. The color of the area against which the stamp is pressed changes gradually, as observed by the optical microscope, indicating the change of the thickness of the silver film as etching proceeds. The final color when etching is complete is blackish, as shown in FIG. **7**.

[0079] FIG. **7** is a series of time-lapse images of the stamping process. In this experiment, FIG. **7**A shows an image immediately prior to etching, FIG. **7**B is midway through etching (about 12 minutes) and FIG. **7**C when etching is substantially complete (about 50 minutes). Prior to the film etching, a cyclic voltammetry characterization of the silver sulfide stamp is performed, the results of which reflect the typical redox potential of Ag/Ag^+ (see FIG. **8**). The increase starting at the valley signifies the onset of redox reactions in the contact surfaces between the silver film, stamp, and the electrode. The area under the curve reflects the Gibb's free energy required to propel this etching process. FIG. **9** shows the change in current over time of the stamping process for four different electric potential differences (0.2V, 0.4V, 0.6V and 0.8V). The current drop during the first few seconds reflects generation of a silver concentration gradient in the stamp that increases the resistance to ionic conduction of the silver ions.

[0080] These experiments validate the feasibility of transferring a pattern from a stamping tool to the surface of a metal, metal layer or a metal film, using electrochemistry. As discussed hereinbelow, using a programmable pattern generation on a solid ionic conductor substrate permits direct writing of features with nano scale line width and micrometer length. The invention also is for active growing and dissolution of nanometer structures via controlled electrical potential application.

EXAMPLE 1

Reprogrammable Patterning of Functional Nanostructures Using Superionic Conduction

[0081] Reprogrammable and reconfigurable active nanostructures and processes influence the functional materials and devices to obtain enhanced energy conversion and chemical sensing. These experiments address outstanding issues in molecular-scale nanofabrication with superionic conduction by: (1) Addressing and explaining the underlying mechanisms of nanoscale charge, mass and energy transport, and reaction kinetics involved in nanostructure formation as a result of ionic conduction in solids; (2) Identifying the factors controlling growth rate and shape fidelity in the grown structures and exploiting this knowledge to develop a highly scalable and reprogrammable, in-parallel transfer stamping process; (3) Exploiting the new capability of programmable and reconfigurable patterning of nanostructures to actively regulate ionic transport and electron flow towards enhanced energy conversion and chemical sensing. The methods disclosed herein utilize reprogrammable nanopatterning. The fundamental understanding of nanostructure growth by ionic conduction and the ability to control it, is further useful for practical design and manufacturing guidelines for compact and efficient energy storage and conversion devices.

[0082] Emerging nanotechnology is increasingly focused on the design and manufacture of nanostructures and nanodevices at scales that involve a few molecules to exploit capabilities and functionalities associated with unique physical and chemical properties identified at these length scales. Qualitatively new behavior often emerges in nanostructured materials due to significant confinement and size effects. New modes of transport for electrical current and/or heat can be obtained when the size of a nanoscale structure becomes less than the characteristic length scale for scattering of electrons or phonons (the mean free path). Similarly the emergence of fundamentally new modes of ionic transport is predicted in nanostructures. Such optimism is supported by dramatically enhanced room-temperature ion conductivity in 1D superlattice systems (Sata et al, 2000) with a characteristic thickness comparable to space charge layers; This opens up new routes to electrochemical devices with enhanced energy conversion and storage density.

[0083] Besides the development of nanoionic devices, such superionic conduction is useful as the basis of efficient and cost-effective processes to produce nanostructures and patterns. Unlike the inefficient and expensive top-down processes and the low-yield nanoimprint lithography processes, superionic conduction can be used as the basis of a manufacturing platform that is efficient, cheap and reprogrammable.

[0084] The invention disclosed herein, enables fast and reversible growth and dissolution of metallic (including, but not limited to, silver) nanoclusters, for active and reprogrammable nanopatterning, based on room-temperature solid ionic (superionic) conductors. Superionic conductors used to design a fast switch (Terabe et al, 2005) suggests that superionic conduction may be ideally suited for the development of both nanoscale processes and devices (e.g. see the switch in FIG. **1** of Terabe et al., 2005). Studies disclosed herein indicate that both additive and subtractive nanomanufacturing are possible with the superionic conduction (see, for example, FIGS. **1**, **3** and **10**).

[0085] FIG. **10**B schematically summarizes use of a prepatterned stamp **70** comprising a solid-state ionic conductor **10** to etch metal **20**. FIG. **10**B illustrates a power supply **35** to energize a cathode **50** and anode **40** to generate an electric field and make recess features **65** on the surface of a metal **20**.

[0086] A comprehensive understanding of the superionic conduction at the nanoscale is useful for formulating and designing nanostructured materials with tunable and controllable ionic conductivity and ion storage density at room temperatures.

[0087] Fabrication and experimental characterization methodology for controllable nanostructure growth/removal with superionic conduction by direct writing of nanopaterns on the superionic conductors. We use an electrochemical atomic force microscope (EC-AFM) to trigger silver growth through ion migration in Ag_2S to demonstrate that nanoscale line patterns can be directly written (FIG. **2**). We also demonstrate that the patterns are erasable with a reversed polarity of applied bias (FIG. **3**). Accordingly, controllable silver nanostructures can be achieved via electrochemical means. To maximize resolution of structures obtained by the methods disclosed herein, superionic conductor substrates preferentially have predictable stoichiometry and low surface roughness. For example, the processes disclosed herein can use superionic conductor substrates comprising single crystal β-Ag_2S as a superionic conductor substrate. A wide variety of superionic conductors can be prepared using state-of-the-art crystal growth facilities. Pressing, slip casting, extrusion, and sintering are examples of other methods used to form polycrystalline or composite superionic conductor substrates.

[0088] Furthermore, understanding and characterizing growth and removal rates as a function of applied potential, regulated tunneling current and environmental temperature further assists in maximizing the resolution and reproducibility of patterns generated by the processes and devices disclosed herein. Depending on the process utilized (e.g. writing versus stamping) growth mechanisms, such as those that occur when growth patterns transition from controlled cluster growth under the electrode to widespread spontaneous growth distributed on the surface of the superionic conductor, vary.

[0089] Many superionic conductors are mixed conductors, conducting both electrons and ions, so that electronic conduction also plays an important role in conduction. To enhance the selectivity of superionic conductors, schemes to limit the electronic current by forming p-n junctions as known in the art can be utilized.

[0090] Because solid state etching at nanoscale is a relatively unexplored area, we use the EC-AFM studies to provide insight to the process mechanisms and limiting factors.

[0091] Mass and charge transport involved in superionic conduction and the growth/dissolution process. While the field of solid state ionics has been an area of major scientific and technological interest in the past, the experimental techniques have primarily focused on bulk material properties. Only very recently was an enhanced room-temperature ion conductivity (>4 orders of magnitude) in 1D layer-by-layer systems reported (Maier, 2000), indicating the emergence of fundamentally new modes of ionic transports with a characteristic thickness comparable to space charge layers. The success of engineering ionic transport in nanoscale confinement opens up new areas of design and manufacturing nanoionic structures and devices with improved efficiency. The benefit of narrowly spaced interfaces that act as fast pathways for ions or components lies not only in the enhanced effective conductivity but also in the possibility of rapid bulk storage resulting from the reduction of the effective diffusion length.

[0092] Theory and modeling of combined ionic and electronic transport and growth kinetics at a wide range of dimensional scales plays a critical role in designing and controlling the growth and dissolution of metal (including silver) nanostructures with molecular scale accuracy. Molecular dynamics and embedding multiscale methods combining quantum-mechanical, atomistic and continuum theories for electrically-mediated fluid/ion flow in nanometer channels assist in understanding the fundamental electrochemical kinetics. Atomic-scale kinetic Monte Carlo methods for simulating surface shape evolution in chemically reactive systems, and developing multiscale modeling methods that treat nanoscale manipulation as a design focus further assist in maximizing the resolution and reproducibility of pattern generation methods and devices disclosed herein. Techniques, ranging from ab initio molecular dynamics, kinetic Monte Carlo, continuum and multiscale theories further assist in exploring the underlying fundamental mechanics such as growth, kinetics and transport properties of silver ions and the combined ion and electron transport due to the applied electric field. Such modeling, in combination with empirical data such as those shown in FIG. **11**, provides greater insight into the underlying fundamental mechanisms.

[0093] Developing reconfigurable and reprogrammable stamping processes with superionic conductors. The coupling of mass and charge transport in ionic conduction leads very naturally to the development of fine resolution etch and deposition processes. The experiments and models disclosed herein provide insight and control of the growth process, upon which reprogrammable stamping tool comprising a superionic conductor is based. FIG. **12**A shows a fixed stamp **70** having an Ag_2S **10** nanostructure combined with limited process control (e.g. applying an electric field between electrodes **40** and **50**, column **55** containing an optional force actuator and electrode) to successfully generate a transfer patterns by etching through a silver film **20** with sub-micron features such as scratches on the stamp surface showing up on the etched substrate, as well as any number of geometrical features. In an embodiment, an elastic material **75**, such as rubber, assists in maintaining uniform pressure between the stamp **70** and metal **20**.

[0094] Reconfigurable and reprogrammable stamps are particularly useful when coupled with real-time sensing and growth control of pattern generation. For example, embedding very precise electronics into the stamp to estimate growth through changes in conductance between the stamp and the substrate, as well as control strategies to overcome the effects of unevenness of stamps by voltage regulation are two examples where reconfiguragable stamps are useful. By manipulating the substrate surface by various types of surface pre-conditioning, the transfer of metal nanostructures onto a variety of materials is possible, thereby ensuring the process summarized in FIG. **12** are widely applicable.

[0095] Design of novel active devices using superionic conduction. Active devices can exploit superionic conduction and be fabricated by the methods disclosed herein. As shown by FIG. **13**, the superionic nanopatterning technology not only fabricates nanostructured fuel cells and batteries with improved ionic conductivity, but also enables novel electrochemically switchable logic and sensing devices useful in an integrated nanoionic systems that is self sustainable from the chemical energy stored or harvested from environment. Here we take the example of an electrochemically tunable plasmonic switch to show the broad application of nanoionic devices.

[0096] As the current architectures of high speed nanoelectronics face challenges of power density and heat management, all optical computation using nanophotonics may provide an alternative route towards parallel information processing at high device densities. The nanopatterning of silver with superionics now offers a potential for novel active and reconfigurable plasmonic device. FIG. **14** shows a schematic for an electrochemically tunable plasmonic switch. The silver nanodots form a plasmonic optical waveguide and because the shape and dimension of the dots made them sensitive to the wavelength and polarization, a plasmonic modulator is realized by dissolving or growing the silver dots at the junctions. The fast and reconfigurable plasmonic interconnect enabled by the superionic conduction provides new architectures for the emerging all-optical computation.

[0097] Characterization of nanoscale superionic conduction and its exploitation in the development of nanoscale superionic devices provides an integrated platform for devices that deal with energy and information. The ability to inexpensively pattern and process functional materials by the present invention at the nanometer scale is an important asset in designing new-generation fuel cells and batteries with integrated systems for sensing and control, and with increased efficiencies that accrue from the exploitation of fundamental phenomena of nanometer scale solid state mass transport and charge separation in energy science.

[0098] Through ionic patterning and switching disclosed herein, understanding of basic mass transport and solid state chemistry at nanometer scales is significantly advanced. This, in turn, assists in optimizing the nanomanufacturing process and tool design, leading to efficient manufacturing and reduced energy consumption. Also, the new manufacturing capabilities, which can ultimately lead to a roll-to-roll type process for nanopatterning, are the basis for new devices and products in photovoltaic and display technology.

[0099] Novel processes for generating sub-hundred nanometer features is presented herein, that integrates and extends the concepts of nanoimprint lithography and electrochemical micromachining. Realized by the mass transport property of solid-state ionic conductors and their dimensional integrity, this technique provides simplicity and high throughput of single-step pattern generation while keeping high feature resolution and reproducibility. Solid-state ionic conductor silver sulfide is chosen and made into a stamping tool on which calibration features are defined to verify the lateral resolution capabilities of this technique. Stamping is achieved under various driving potentials and sub-hundred-nanometer lateral resolution is obtained. Even without optimization of the process parameters and environmental factors, this direct patterning technique shows the potential to achieve single-step transfer of sub-hundred nanometer feature with low energy consumption, as well as the flexibility to be integrated with other nano-fabrication techniques for applications such as chemical sensors and photonic structures.

EXAMPLE 2

Direct Nanopatterning with Solid Ionic Stamping

[0100] FIG. **15**A is an SEM image of an Ag_2S solid state ionic conductor stamp used for electrochemical stamping and FIG. **15**B an SEM image of the corresponding pattern etched in Ag metal.

[0101] This example discloses an embodiment for generating sub-hundred nanometer features that integrates and extends the concepts of nanoimprint lithography and electrochemical micromachining. Realized by the mass transport property of solid-state ionic conductors and their dimensional integrity, this technique provides simplicity and high throughput of single-step pattern generation while keeping high feature resolution and reproducibility. In an embodiment, the solid-state ionic conductor is silver sulfide and is made into a stamping tool on which calibration features are defined to verify the lateral resolution capabilities of this technique. Stamping is achieved under various driving potentials and sub-hundred-nanometer lateral resolution is obtained. Even without optimization of the process parameters and environmental factors, this direct patterning technique achieves single-step transfer of sub-hundred nanometer feature with low energy consumption, as well as the flexibility to be integrated with other nano-fabrication techniques for applications such as chemical sensors and photonic structures.

[0102] Surface micromachining of sub-micron features plays a substantial role in the fabrication of a wide variety of sensor devices and microelectromechanical system (MEMS) components. These techniques realize the generation of such features through either removing material from substrate, top-down etching, or adding materials, bottom-up deposition, to build up the desired features. Among the “top-down” fabrication techniques nanoimprint lithography followed by dry/wet etching, and electrochemical machining (EM) provides features with size down to tens of nanometers. Nanoimprint lithography followed by chemical/physical etching of substrate provides high feature geometrical and dimensional integrity at the expanse of multi-step, complex lithography processes that require stringent process environment control and high-cost equipments.

[0103] The novel patterning technique presented herein extends the concepts of state-of-the-art nanoimprint lithography and electrochemical micromachining. The solid ionic stamping demonstrated in this example exploits the mass-transfer property of solid state ionic conductors to produce sub-hundred-nanometer features with high throughput and reproducibility.

[0104] Electrochemical machining that utilizes the local dissolution of metallic substrate ions and mass transport in the etching medium by liquid electrolye, can achieve nanometer feature generation with relatively process simplicity and low cost. The feature-transfer fidelity, however, degrades as feature size reduces. As feature approaches the limits where the necessary replenishment of liquid electrolyte etching medium becomes limited, features like sharp edges and thin lines lose their geometrical and dimensional integrity when transferred from machining tool to substrate surface.

[0105] In an embodiment the present invention uses solid ionic stamping. The solid ionic stamping presented herein, in contrast to current electrochemical machining techniques, provides high feature geometrical and dimensional fidelity in generating the desired metallic feature using a relatively simple single-step feature transfer. In addition, the process is low cost while eliminating the need for sophisticated process equipment while maximizing feature-transfer fidelity due to the physical property nature of the etching medium and stamp. The electrochemical stamp using a solid state ionic conductor stamp of the present invention also avoids the need for post-treatment of the etching medium used for metal etching.

[0106] FIG. **16** is a schematic of an embodiment for ionic migration of silver species in a solid state ionic conductor, silver sulfide. When subjected to an electric field applied across a silver **20** -silver sulfide **10** interface through anode **50** and cathode **40** attached to them respectively, silver atoms oxidize into mobile ions **42** and electrons **44**. Mobile silver ions **42** move from the interface through the conduction channels formed in the silver sulfide bulk **10**, toward the cathode **50**. Upon receiving electrons **44** when reaching the cathode surface, silver ions reduce back to atoms **43** and deposit on the interface between the cathode **50** and Ag_2S **10**. The oxidation reaction at the interface between metal **20** (e.g. anode) and Ag_2S **10** is used as a tool for surface micromachining. The advantage of using solid state ionic conductors is that mass transport only occurs at the surfaces of film metal anode and solid ionic conductor where physical contact exists, making it an ideal tool for pattern transfer. In this work, silver sulfide is synthesized and formed into a tool having a patterned surface, including nano-scale dimensioins, for use as a stamp **70** to perform surface micromachining on a silver substrate. The stamp **70** etches metal **20** resulting in a pattern of etched recess feature **65** (FIG. **16**C).

[0107] Mass transport coupled with ionic migration in electrolyte subjected to electrical field, have been used to develop patterning techniques and devices. A quantized conductance atomic switch that has been developed wherein silver mobile atoms bridge and open a tunneling gap between Pt and silver sulfide wires when driven by a gate potential. Such a switch is reported to be capable of operating at 1 MHz with low a driving voltage of 0.6V, adding another nano-scale switch operating at high frequency yet low energy consumption. With the same ionic mass transport concept, nanopatterning techniques have been developed to achieve sub-hundred nanometer line writing and dot deposition with scanning probe microscopy. These techniques utilize the electric potential applied across a scanning probe and desired substrate surface and the migration of metal ions from a solid-state ionic conductor forming either the substrate or scanning tip to realize the generation of single line writing or metal dots deposition. The practicality of this direct pattern writing is limited by the low throughput and high complexity and cost of the instrumentation involved. With the aid of a high strength tool material like Tungsten, the resolution of electrochemical machining has been pushed to the sub-hundred nanometer regime. The pattern dimension fidelity and pattern geometry of the transferred feature, however, is limited by the current density distribution in the liquid-state electrolyte and its physical properties.

[0108] Lithographic processes followed by chemical/physical etching of metal have been developed to a point where the cost is minimized and process standardized to maximize the yield. Those processes remain expensive, however, as skilled personal and chemical handling and waste treatment are essential to the operation of the multi-step processes.

[0109] The present invention described herein extends the application of mass transport properties of electrolyte to far beyond the generation of simple geometrical pattern generation with complex scanning microscopy systems. Instead, the patterns created are intricate two and three-dimensional patterns in the sub-hundred nanometer scale within a single-step, high throughput process.

[0110] Silver sulfide synthesis/stamp preparation. An electrochemical cell is designed to perform the synthesis of silver sulfide crystals. The cell is composed of a 6 mm-ID quartz tube with both ends open. In the tube a silver iodide pellet pressed from powder is placed in contact with a silver pellet on one side which allows the transport of silver ions from silver across silver iodide, and the other side exposed to sulfur which allows silver ions to react with sulfur. A cell potential of 800 mV is then applied through two electrodes attached to the free surfaces of silver and silver iodide pellets when the cell reached a reaction temperature of 360 degrees centigrade. At these reaction conditions silver ions then migrated through silver iodide layer to cathode and reacted with sulfur, forming a silver sulfide pellet of a few millimeters thick. The reaction proceeded until the cell current dropped to a steady value, indicating the end of reaction, and was then cooled to room temperature.

[0111] Another method is also employed for silver sulfide synthesis. A glass tube is filled with sulfur and pressed against a silver pellet sitting in a glass test tube. The tube is then heated to 400 degrees centigrade to allow silver-sulfur reaction. The glass tube pressed against the silver pellet prevents further growth of the porous silver sulfide layer closer to the silver side in the formation of silver sulfide layer, and promotes the desired dense silver sulfide near the sulfur side to further increase thickness. The synthesized silver sulfide can be as thick as centimeters, depending on the amount of silver and sulfur available. The synthesized silver sulfide pellet is then shaped and patterned with focused ion beam to be used in the subsequent solid ionic stamping. Calibration features are made such that the resolution limits are explored. Silver substrate is prepared with a 250 nm-thick silver film deposited with electron beam evaporation on a 300-μm thick glass cover slip. The silver substrate is electrically connected to an electrode through physical contact with a copper electrode. The surface area of the metal substrate facing the solid state ionic conductor can have any value, including a range from about 100 μm^2 to about 5 mm^2.

[0112] Silver sulfide stamp characterization. Before patterning with FIB, the synthesized silver sulfide stamp is characterized with x-ray diffraction ("XRD") for composition and cyclic voltametry for electrochemical response. The XRD is conducted on a Rigaku D-Max system with a scanning range (2-theta) from 0 to 60 degrees and a scan rate of 1.5 degrees per minute. XRD diffractogram are overlaid and compared with standard peaks from powder form silver sulfide. The results confirm the composition of synthesized silver sulfide. The silver sulfide stamp is then characterized with cyclic voltametry running at 0.5 Hz with a range from positive 2 volts to negative 2 volts. Characteristic histeresis confirm the electrochemical behavior of synthesized silver sulfide.

[0113] Solid state electrochemical etching. Solid-state etching is performed at room temperature at 1 atmospheric pressure. The prepared silver sulfide stamp is attached to a platinum electrode which is fixed to a micro-stage for positioning. On another micro-stage silver substrate is fixed onto a quartz window with a platinum electrode attached to it. An optical microscope is built and placed on the back side of the quartz window for positioning and process monitoring. Solid ionic stamping is performed by bringing the stamp in contact with the silver substrate and the polarity of the electric field is chosen such that silver is the anode and the Ag_2S side electrode is cathode. Different electrical potentials ranging from 0.2 V to 0.8 V with an interval of 0.2 V are applied and current monitored with a Potentialstat. The processes are also optically monitored with an optical microscope observing from the back side of the quartz window upon which the silver substrate resides. The silver film thickness decreased as stamping proceeded, leading to a continued chromatic change in the optical image of the film. After stamping, the silver substrate is then characterized with Atomic Force Microscopy (AFM) and Scanning Electron Microscope (SEM).

[0114] Solid-state electrochemical etching: Etch kinetics.

[0115] It is known that the ionic conduction of silver sulfide is a contribution from solubility of silver in silver sulfide. Shown in FIG. **17** is the cyclic voltametry of the silver sulfide stamp measured between two platinum electrodes. The two humps on the ramp-up and ramp-down curves correspond to the increase in overall conductivity induced by the migration of excessive silver in silver sulfide, confirming the electrochemical behavior of synthesized Ag_2S. When a potential field is built up across the silver sulfide stamp, the migration of the excessive silver in the stamp along the direction of the field and the polarization effect resulting from the silver concentration gradient due to silver migration start to take place. These two effects counteract each other—as more silver ions become mobile charge carriers and move from the anode side to the cathode side of the silver sulfide stamp, the concentration of silver in silver sulfide reduces while the concentration on the cathode side increases. This concentration gradient then builds up a polarization effect within the stamp which acts as a resistive force to the migration of silver ions. As potential keeps increasing, the polarization effect also keeps growing to the point where the ionic current is completely blocked, resulting the current drop on the CV diagram. For this reason, it is thought that the maximum ionic mass transport efficiency occurs at the potential where the corresponding current peaks out.

[0116] FIG. **18** shows the current monitored over etching time for different driving potentials. The currents monitored in this experimental setup are the combined effects of ionic and electrical current, due to the mixed-conduction nature of silver sulfide. Currents for different voltage level follow the same trend—they reach their highest value within the fist stage of etching, slope down to lower values in the second stage, and then at the last stage drop to a steady-low value, indicating the end of etching. The three-stage behavior can be explained in a similar manner as is in explaining the CV diagram: During the first and the second stage, three effects play different roles that contribute to the overall current output. The increase in silver concentration due to the dissolved silver from silver substrate into the silver sulfide stamp increases the ionic current. At the same time, the growing polarization effect gradually increases, thereby reducing the mobility of silver ions, contributing an increasing reduction in the ionic current. As the concentration reaches the solubility limits of silver in silver sulfide, a steady-state is reached where further dissolution of silver into silver sulfide from the anode results in a reduction of silver ion to silver atoms depositing on the cathode, facilitating the advance of negative stamping. At the start of the last stage, the depletion of silver on the anode side results in the reduction and eventually the elimination of ionic current, leaving the current pure electrical. This is a good indication of the end of etching.

[0117] Resolution: Depth of features & sidewall angles.

[0118] FIG. **19** is a side by side comparison of the silver sulfide stamp and the produced silver feature. As seen in FIGS. **19**A and **19**B (the stamp) and **19**C (the etched substrate), all the geometrical features are successfully transferred—part of the silver film is removed through contact with the flat surface area on the silver sulfide stamp, leaving behind the structures corresponding to the recess area made on silver sulfide tool. The lateral resolution achieved is 90 nm on a straight line, calibrated with AFM. The height of the silver features remains at 250 nm, the silver film thickness prior to etch, confirming that the bottom surface of the recess features on silver sulfide is not in contact with the silver substrate during the process.

[0119] Line widths of the recess feature on the silver sulfide stamp and the finished silver pattern are calibrated with AFM and recorded. The generated feature on the etched pattern has a lateral shrinkage as compared to the designed feature size on the silver sulfide stamp. The etched feature has a tendency to have a smaller dimension than that expected from stamp. FIG. **20** shows the lateral shrinkage for different line widths. For the four driving potential tested, 0.6V has the lowest lateral shrinkage over the entire size range while 0.2V and 0.4V have higher lateral dimension reduction. For the smallest designed line width, 110 nm, the feature comes out to be 95 nm, a 13% reduction, for 0.6V; whereas the lateral reductions for 0.2V and 0.4V are 21% and 34% respectively. Without wishing to be bound to any particular theory, this effect is believed to be caused by the electrostatic force between stamp pattern side walls and the resulting silver features, which pulls silver grains out of the silver feature across the gap that is formed as stamping proceeds. As the gap increases to the size where the electrostatic force is small enough to be balanced by the bind force between silver grains, the remaining silver stays stable. Generating plots such as those shown in FIG. **20**, allows for compensation in the stamp size lines so as to obtain lines in the etched material of a given dimension.

[**0120**] Stamping cycle time. As shown in FIG. **18**, the current drops to a steady lower value when all the excess silver dissolved in silver sulfide and the silver film in contact with silver sulfide stamp is depleted, indicating the end of etching process. The etch rate is calculated at different driving potentials and presented in FIG. **21**. The etch rate ranges from 0.7 nm per second at 0.2V to 2.2 nm per second at 0.8V, comparable to conventional dry etching of silver. The power consumption of this solid ionic stamping, however, is orders of magnitude less then those dry etching techniques.

[**0121**] Surface roughness and resolution. Also shown in FIG. **21** is the surface roughness of the resulting etched silver structure for different driving potentials. The surface roughness is measured by AFM in 1 micron square. Although the process driving potential does not have strong effect on the roughness of the etched surface, at 0.4V and 0.6V the resulting silver surface is relatively less rough.

[**0122**] Effect of reusing the stamp. Reusing the stamp causes the features of 50 nanometer lines to collapse. This effect is believed to be caused by the repeated mechanical contact of the silver sulfide stamp and silver surface and the force when the two surfaces are engaged. The force is regulated by setting a fix position to which the stage controlling the stamp moves in every run of experiment. Reuse of the stamp does not show strong effects on the roughness of the stamp; it remains the same after the stamp has been use for 8000 seconds on actual etching time.

EXAMPLE 3

Electrochemical Stamping

[**0123**] The invention disclosed herein provides a unique and new capability to pattern metals with sub-100 nm resolution in a high-through put stamping process. For example, FIG. **22** shows arrays of patterns can be etched in metal. Depending on manufacturing considerations, such a 5×5 array may be created using single step electrochemical stamping, or alternatively, the metal may be repeatedly stamped to obtain the array. FIG. **23** shows the stamps of the present invention provide structures having sub-100 nm resolution. For example, multiple distinct lines or channels are generated that are separated by 50 nm and the lateral resolution is 60 nm. In an embodiment, the process is a solid-state, room temperature process that is highly compatible with a large variety of process technologies. Although the examples provided herein utilize silver, different ionic crystals for other materials, including but not limited to copper, and gold, can be similarly used, to obtain patterns composed of these other materials.

Statements Regarding Incorporation by Reference and Variations

[**0124**] All references cited throughout this application, for example patent documents including issued or granted patents or equivalents; patent application publications; and non-patent literature documents or other source material are hereby incorporated by reference herein in their entireties, as though individually incorporated by reference, to the extent each reference is at least partially not inconsistent with the disclosure in this application (for example, a reference that is partially inconsistent is incorporated by reference except for the partially inconsistent portion of the reference).

[**0125**] Every formulation or combination of components described or exemplified herein can be used to practice the invention, unless otherwise stated.

[**0126**] Whenever a range is given in the specification, for example, a temperature range, a size range, a conductivity range, a time range, or a composition or concentration range, all intermediate ranges and subranges, as well as all individual values included in the ranges given are intended to be included in the disclosure. It will be understood that any subranges or individual values in a range or subrange that are included in the description herein can be excluded from the claims herein.

[**0127**] All patents and publications mentioned in the specification are indicative of the levels of skill of those skilled in the art to which the invention pertains. References cited herein are incorporated by reference herein in their entirety to indicate the state of the art as of their publication or filing date and it is intended that this information can be employed herein, if needed, to exclude specific embodiments that are in the prior art.

[**0128**] As used herein, "comprising" is synonymous with "including,""containing," or "characterized by," and is inclusive or open-ended and does not exclude additional, unrecited elements or method steps. As used herein, "consisting of" excludes any element, step, or ingredient not specified in the claim element. As used herein, "consisting essentially of" does not exclude materials or steps that do not materially affect the basic and novel characteristics of the claim. In each instance herein any of the terms "comprising", "consisting essentially of" and "consisting of" may be replaced with either of the other two terms. The invention illustratively described herein suitably may be practiced in the absence of any element or elements, limitation or limitations which is not specifically disclosed herein.

[**0129**] One of ordinary skill in the art will appreciate that starting materials, materials, reagents, synthetic methods, purification methods, analytical methods, assay methods, and methods other than those specifically exemplified can be employed in the practice of the invention without resort to undue experimentation. All art-known functional equivalents, of any such materials and methods are intended to be included in this invention. The terms and expressions which have been employed are used as terms of description and not of limitation, and there is no intention that in the use of such terms and expressions of excluding any equivalents of the features shown and described or portions thereof, but it is recognized that various modifications are possible within the scope of the invention claimed. Thus, it should be understood that although the present invention has been specifically disclosed by preferred embodiments and optional features, modification and variation of the concepts herein disclosed may be resorted to by those skilled in the art, and that such modifications and variations are considered to be within the scope of this invention as defined by the appended claims.

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We Claim:

1. A method of making a structure comprising:

a. providing a first electrode in electrical contact with a solid state ionic conductor;

b. providing a second electrode in electrical contact with a metal;

c. establishing electrical contact between at least a portion of said solid state ionic conductor and said metal; and

d. generating an electric field between said first and second electrodes, wherein a portion of the metal is oxidized thereby generating metal ions and free electrons, wherein said metal ions migrate through the solid state ionic conductor to the first electrode where they are reduced and wherein said free electrons migrate to said second electrode, thereby making said structures;

wherein said solid state ionic conductor or said first electrode is a stamping tool that generates a pattern of electrical contacts between said stamping tool and said solid state ionic conductor or said metal.

2. The method of claim 1 wherein the metal comprises a metal layer, a bulk metal, metal particles, metal cluster or a metal substrate.

3. The method of claim 1 wherein the solid state ionic conductor comprises metal atoms that are the same as metal atoms in said metal.

4. The method of claim 1 wherein said electric field is generated by applying a potential difference between said first and second electrodes, wherein said second electrode has a higher electrical potential than said first electrode.

5. The method of claim 4 wherein said potential difference between first and second electrodes has a value selected from the range of about 100 mV to about 2000 mV.

6. The method of claim 1 wherein said first electrode is a cathode and wherein said second electrode is an anode.

7. The method of claim 1 wherein physical contact is established between at least a portion of said stamping tool and said solid state ionic conductor or said metal.

8. The method of claim 1 wherein said stamping tool comprises a pattern of relief features, wherein physical or electrical contact between at least a portion of said relief features and said solid state ionic conductor or said metal generates said pattern of electrical contacts.

9. The method of claim 8 wherein said pattern of said stamping tool is at least partially transferred to said ionic conductor via electrochemical etching or said metal via electrochemical deposition.

10. The method of claim 1 further comprising the step of applying a force to said stamping tool.

11. The method of claim 10 wherein said force is applied uniformly to one or more surfaces of said stamping tool such that electrical contact between at least a portion of said stamping tool and said solid state ionic conductor or said metal is maintained during processing.

12. The method of claim 1 wherein said ionic conductor is said stamping tool, wherein said stamping tool has a selected pattern of relief features, wherein physical contact between at least a portion of said relief features and said metal generates said pattern of electrical contacts.

13. The method of claim 12 wherein metal atoms are oxidized in regions of said metal in physical contact with at least a portion of said relief features of said stamping tool.

14. The method of claim 12 wherein localized electrochemical etching of said metal occurs at regions of said metal in physical contact with said relief features of said stamping tool.

15. The method of claim 12 wherein at least a portion of said pattern of said stamping tool is transferred to said metal via electrochemical etching.

16. The method of claim 12 wherein at least a portion of said relief features of said stamping tool are nanosized relief features, microsized relief features or both nanosized features and microsized relief features.

17. The method of claim 1 wherein said first electrode is said stamping tool, wherein said stamping tool has a shape selected such that electrical contact between said stamping tool and said solid state ionic conductor generates said pattern of electrical contacts.

18. The method of claim 17 wherein said metal ions are reduced at regions of said solid state ionic conductor in electrical contact with said stamping tool, thereby generating one or more deposited metal layers on a surface of said solid state ionic conductor in electrical contact with said stamping tool.

19. The method of claim 17 wherein localized electrochemical deposition of metal occurs at regions of said solid state ionic conductor in electrical contact with said stamping tool.

20. The method of claim 17 wherein said stamping tool comprises a plurality of features arranged in a selected pattern, and wherein at least a portion of said pattern of said stamping tool is transferred to a surface of said solid state ionic conductor via localized electrochemical deposition.

21. The method of claim 20 wherein said features of said stamping tool are nanosized features, microsized features or both.

22. The method of claim 20 wherein said features of said stamping tool have substantially the same voltages.

23. The method of claim 20 wherein at least a portion of said features of said stamping tool have substantially different voltages.

24. The method of claim 20 wherein said stamping tool comprises an array of individually addressable electrodes in electrical contact with said solid state ionic conductor, wherein the voltage on each electrode in the array is independently selectable.

25. The method of claim 24 wherein said stamping tool is capable of transferring a pattern to a surface of said solid state ionic conductor that is programmable, scalable or both programmable and scalable.

26. An electrochemical patterning system for making one or more structures, comprising:

a first electrode in electrical contact with a solid state ionic conductor; and

a second electrode in electrical contact with a metal, wherein at least a portion of said solid state ionic conductor and said metal are in electrical contact, wherein said solid state ionic conductor or said first electrode is a stamping tool that generates a pattern of electrical contacts between said stamping tool and said solid state ionic conductor or said metal.

27. The system of claim 26 wherein said wherein solid state ionic conductor and said metal are in electrical contact such that generation of an electric field between said first and second electrodes results in oxidation of a portion of said metal, thereby generating metal ions and free electrons, wherein said metal ions migrate through the solid state ionic conductor to the first electrode where they are reduced and wherein said free electrons migrate to said second electrode.

28. The system of claim 26 wherein at least a portion of said solid state ionic conductor and said metal are in physical contact.

29. The system of claim 26 wherein said metal layer is said second electrode.

30. The system of claim 26 further comprising an actuator operationally connected to said stamping tool such that it is capable of providing a force to said stamping tool that maintains electrical contact between said stamping tool and said solid state ionic conductor or metal.

31. The system of claim 26 wherein said stamping tool has a Young's modulus selected from the range of about 20 GPa to about 200 GPa.

32. The system of claim 26 wherein said first electrode is a cathode and said second electrode is an anode.

33. The system of claim 26 wherein said ionic conductor is said stamping tool, wherein said stamping tool has a selected pattern of relief features, wherein at least a portion said relief features of said stamping tool are provided in physical contact with said metal, thereby generating said pattern of electrical contacts.

34. The system of claim 33, wherein application of an electric field between said first and second electrodes transfers at least a portion of said pattern of said stamping tool to said metal layer via electrochemical etching.

35. The system of claim 33 wherein at least a portion of said relief features of said stamping tool are nanosized relief features, microsized relief features or both nanosized features and microsized relief features.

36. The system of claim 26 wherein said first electrode is said stamping tool, wherein said stamping tool comprises a plurality of features arranged in a selected pattern, wherein at least a portion of said features are in electrical contact with said solid state ionic conductor thereby generating said pattern of electrical contacts.

37. The method of claim 36 wherein application of an electric field between said first and second electrodes transfers at least a portion of said pattern of said stamping tool to said solid state ionic conductor via electrochemical deposition.

38. The system of claim 36 wherein said features of said stamping tool have substantially the same voltages.

39. The system of claim 36 wherein at least a portion of said features of said stamping tool have substantially different voltages.

40. The system of claim 36 wherein said stamping tool comprise a grid electrode.

41. The system of claim 36 wherein said stamping tool comprises an array of individually addressable electrodes in electrical contact with said solid state ionic conductor, wherein the voltage on each electrode in the array is independently selectable.

42. The system of claim 36 wherein said stamping tool is programmable, scalable or both programmable and scalable.

43. The system of claim 26 wherein said metal has a thickness selected from the range of about a few nanometers to about 100 mm, and wherein said solid state ion conductor has a thickness selected from the range of about 50 nanometers to about 100 mm.

44. The system of **26** wherein said solid state ion conductor has an ionic conductivity selected from the range of about 0.001 S/cm to about 440 S/cm.

45. The system of **26** wherein said solid state ion conductor is selected from the group consisting of Ag_2S, Cu_2S, AgI, $RbAg_4I_5$, Ag_3SI, AgCuS, AgCuSe, $Br_4Cu_{16}I_7Cl_{13}$, and Cu_2S.

46. The system of claim 26 wherein said solid state ion conductor is an amorphous solid, a semicrystalline solid, a single crystalline solid, or a composite material.

47. The system of claim 26 wherein said solid state ion conductor is a superionic conductor.

48. The system of **26** wherein said metal is selected from the group consisting of Ag, Cu, Au, Zn, and Pb.

49. An electrochemical stamping tool for etching structures into a metal comprising:

a first electrode having a first electric potential;

an ionic conductor having a selected pattern of relief features, wherein said ionic conductor is in electrical contact with said first electrode and wherein at least a portion of said relief features are capable of establishing electrical contact with said metal; and

a second electrode in electrical contact with said metal having a second electric potential that is higher than said first electrode.

50. An electrochemical stamping tool for generating structures on a solid state ionic conductor comprising:

a first electrode comprising a plurality of features arranged in a selected pattern, wherein at least a portion of said features are capable of establishing electrical contact with said solid state ionic conductor; and a metal in electrical contact with said solid state ionic conductor.

51. The electrochemical stamping tool of claim 50 wherein said first electrode is an array of electrodes, wherein at least a portion of the electrodes in the array are in electrical contact with said solid state ionic conductor.

52. A method of making a structure comprising:

a. providing a first electrode in electrical contact with a metal and in electrical contact with a solid state ionic conductor, wherein said metal covers at least a portion of a surface of said solid state ionic conductor;

b. providing a second electrode in electrical contact with said solid state ionic conductor;

c. establishing electrical contact between at least a portion of said solid state ionic conductor and said metal; and

d. generating an electric field between said first and second electrodes, wherein metal atoms in said metal are oxidized, thereby generating metal ions and free electrons, wherein said metal ions migrate through said solid state ionic conductor to said second electrode where they are reduced and wherein said free electrons migrate to said first electrode, thereby making said structures.

53. The method of claim 52 wherein said metal comprises a metal surface, bulk metal, metal substrate, metal cluster or metal particles.

54. The method of claim 52 wherein the electrical contact between said first electrode and said metal is a single point contact.

55. The method of claim 52 wherein the electrical contact between said first electrode and said metal is an electrical contact pattern.

56. The method of claim 55 wherein said electrical contact pattern is generated by a stamping tool.

57. The method of claim 55 wherein said electrical contact pattern is generated by said first electrode having a plurality of features arranged in a selected pattern, and wherein at least a portion of said pattern is transferred to a surface of said metal via localized electrochemical etching.

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