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(54) **Title:** LIGHT-DIRECTED ELECTROCHEMICAL PATTERNING OF COPPER STRUCTURES

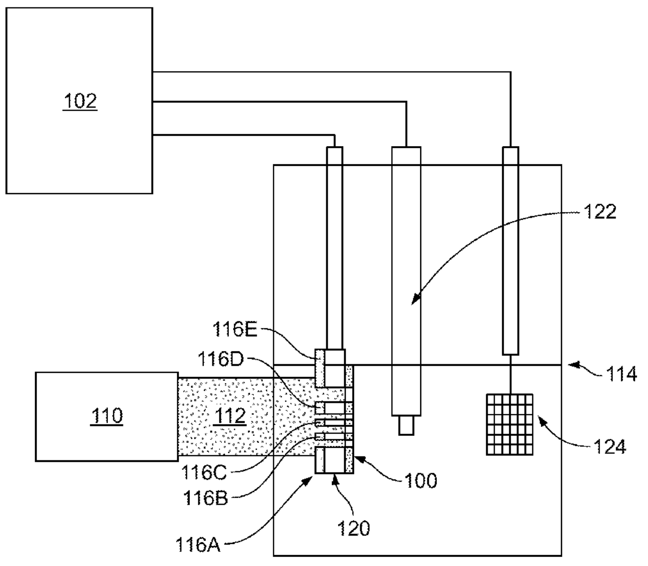

FIG. 1

(57) **Abstract:** A method creating a patterned film with cuprous oxide and light comprising the steps of electrodepositing copper from a solution onto a substrate; illuminating selected areas of said deposited copper with light having photon energies above the band gap energy of 2.0eV to create selected illuminated sections and non-illuminated sections; and stripping non-illuminated sections leaving said illuminated sections on the substrate. An additional step may include galvanically replacing the copper with one or more noble metals.

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[Continued on next page]

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LIGHT-DIRECTED ELECTROCHEMICAL PATTERNING OF COPPER STRUCTURES

RELATED APPLICATIONS

[0001] This application claims the benefit of U.S. Provisional Application No. 62/380911 filed August 29, 2016, and herein incorporated by reference.

FIELD OF THE INVENTION

[0002] Cuprous oxide (Cu_2O) is considered to be an ideal semiconductor for solar or photoelectrochemical cells because it has a small (2.0eV), direct band gap, is composed of inexpensive and earth abundant materials, and can be synthesized by electrodeposition or oxidation of Cu metal. Copper and its oxides are also an interesting material system because it can easily be oxidized, reduced, or dissolved electrochemically by choice of electrochemical potentials and pH of aqueous solution.

[0003] Copper is also an important material for developing and patterning circuits. A current practice to pattern copper in circuits utilizes expensive photolithography or direct-write methods like laser ablation.

BRIEF SUMMARY OF THE INVENTION

[0004] In one embodiment, the present invention provides an inexpensive method to pattern copper and oxide structures using direct lithographic processes driven by illumination. This eliminates the need for expensive lasers, photoresist chemistry, or chemical/physical vapor deposition facilities. It requires low power and illumination coherence constraints, making it an inexpensive alternative to current methods. Moreover, as copper is an increasingly expensive raw material, all of the copper not used in the patterning is available for other uses.

[0005] In another embodiment, the present invention provides patterning via direct illumination with no expensive photosensitive chemistry required.

[0006] In yet another embodiment, the present invention provides an inexpensive electrodeposition process, with no expensive evaporation processes required.

[0007] In yet another embodiment, the present invention provides an inexpensive electrodeposition process, with no expensive vacuum processes required.

[0008] In another embodiment, the present invention provides patterning processes which use incoherent light sources which reduce the need for high-power lasers to perform patterning.

[0009] In another embodiment, the present invention provides methods for patterning copper that may be generalizable to any conductive substrate (not just transparent ones).

[00010] In another embodiment, the present invention provides methods that use dark and transparent Cu_2O which are chemically distinct phases to pattern thin films features including sub-millimeter features.

[00011] In yet another embodiment, the present invention provides methods that galvanically replaces deposited Cu_2O pattern with one or more metals such as noble metals to create a pattern consisting of the substituted metal or metals. In a preferred embodiment, the metal is a noble metal.

[00012] In another embodiment, the present invention provides methods that direct write copper-based structures on electrodes to either pattern regions of Cu_2O or to pattern conductive Cu patterns for circuits that replace photolithography in compatible materials systems, which is the current method by which copper is patterned.

[00013] Additional objects and advantages of the invention will be set forth in part in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention will be realized and attained by means of the elements and combinations particularly pointed out in the appended claims.

[00014] It is to be understood that both the foregoing general description and the following detailed description are exemplary and explanatory only and are not restrictive of the invention, as claimed.

BRIEF DESCRIPTION OF THE SEVERAL VIEWS OF THE DRAWINGS

[00015] In the drawings, which are not necessarily drawn to scale, like numerals may describe substantially similar components throughout the several views. Like numerals having different letter suffixes may represent different instances of substantially similar components. The drawings illustrate generally, by way of example, but not by way of limitation, a detailed description of certain embodiments discussed in the present document.

[00016] Figure 1 is a schematic of a deposition procedure that may be used for an embodiment of the present invention.

[00017] Figure 2A provides an example of direct illuminated writing of black cuprous oxide (illuminated area) and plain, yellow cuprous oxide (masked area) via potentiostatic electrodeposition for an embodiment of the present invention.

[00018] Figure 2B illustrates a reflection image of direct illuminated writing of cuprous oxide (illuminated area) with cathodic electrodeposition/anodic dissolution for an embodiment of the present invention.

[00019] Figure 2C illustrates a back-illuminated image of direct illuminated writing of cuprous oxide (illuminated area) with cathodic electrodeposition/anodic dissolution for an embodiment of the present invention.

[00020] Figure 3A is a schematic of the photolithographic patterning of Cu_2O on a conductive surface for an embodiment present invention.

[00021] Figure 3B depicts the galvanic replacement of Cu_2O with Au, Ag, or other noble metals that spontaneously form on the surface while oxidizing the Cu_2O back to soluble Cu2+ ions for an embodiment present invention.

[00022] Figure 4A shows a time series of Cu 2p and spectra for Cu_2O films submerged in a Galvanic replacement reaction (GRR).

[00023] Figure 4B shows a time series of Au 4f XPS spectra for Cu_2O films submerged in 5mM NaAuCl4 GRR solution for an embodiment present invention.

[00024] Figure 5A is a comparison of Cu 2p spectra for Cu_2O films submerged in an aqueous buffer for an embodiment present invention.

[00025] Figure 5B is a comparison of Au 4f XPS spectra for Cu_2O films submerged in an aqueous buffer for an embodiment present invention.

[00026] Figure 6A is a SEM micrograph of the nanoscale of GRR-deposited Au on Cu2O after 5-minute exposure for an embodiment present invention.

[00027] Figure 6B is a SEM micrograph of the nanoscale microstructure of GRR-deposited Au on Cu2O after 5-minute exposure for an embodiment present invention.

[00028] Figure 7A illustrates GRR-deposited Au on Cu_2O without illumination as shown in Figure 4A.

[00029] Figure 7B illustrates GRR-deposited Au on Cu_2O with 455nm LED illumination but without NaAuCl4 in the solution for an embodiment present invention.

[00030] Figure 7C illustrates GRR-deposited Au on Cu_2O and with 455nm LED illumination and with NaAuCl4 in the solution for an embodiment present invention.

DETAILED DESCRIPTION OF THE INVENTION

[00031] Detailed embodiments of the present invention are disclosed herein; however, it is to be understood that the disclosed embodiments are merely exemplary of the invention, which may be embodied in various forms. Therefore, specific structural and functional details disclosed herein are not to be interpreted as limiting, but merely as a representative basis for teaching one skilled in the art to variously employ the present invention in virtually any appropriately detailed method, structure or system. Further, the terms and phrases used herein are not intended to be limiting, but rather to provide an understandable description of the invention.

[00032] As shown in Figure 1, in one embodiment of the present invention, cuprous oxide (Cu_2O) 100 can be electrodeposited from a solution of copper sulfate by using a potentiostat 102, light source 110 which may be a light emitting diode that is used to create a light pattern 112, electrolyte solution 114, and mask 116A-116E which may be transparent. Also provided are electrode 120, which may be transparent or non-transparent, reference electrode (RE) 122, and counter electrode (CE) 124.

[00033] In a preferred embodiment, cuprous oxide (Cu_2O) can be electrodeposited from a solution of copper sulfate and lactic acid, adjusted to basic pH (9-13) with sodium hydroxide. The electrodeposition is carried out on a conductive substrate like fluorine-doped tin oxide on glass, metal-coated substrates like evaporated gold on glass, or a silicon wafer as well as other substrates to which the metal will adhere.

[00034] As shown, a cathodic potential is applied to the electrode in solution (roughly -0.4V vs. Ag/AgCl reference electrode) to reduce the copper ions in solution and form the solid Cu_2O phase as a thin-film coating on the surface of the electrode. Cuprous oxide is synthesized as its hole-doped, p-type photoactive phase in this process. Moreover, it is a photocathode, meaning that the minority carrier electrons that are transferred at the interface to drive the electrodeposition can also be excited by light absorption to drift to the interface.

[00035] It has been found that the electrons are energetic enough to reduce Cu_2O on the surface to Cu as a method of photodoping. As a result, the regions of the thin film grown under illumination are visibly and chemically different than the regions grown without illumination as shown in Figures 2A-2C.

[00036] Figure 2A provides an example of direct illuminated writing of black cuprous oxide (illuminated area) 200 and plain, yellow cuprous oxide (masked area) 202 via potentiostatic electrodeposition for an embodiment of the present invention. Figure 2B illustrates a reflection image of direct illuminated writing of cuprous oxide (illuminated area) 210 with cathodic electrodeposition/anodic dissolution for an embodiment of the present invention.

[00037] Figure 2C illustrates a back-illuminated image of direct illuminated writing of cuprous oxide (illuminated area) 220 with cathodic electrodeposition/anodic dissolution for an embodiment of the present invention. As a result, the methods provided by the present invention provide methods to grow copper structures patterned by illumination.

[00038] The electrode can be switched between the cathodic (depositing) potential and a slightly anodic (dissolving) potential. The illumination of the pattern may

occur during, before or in-between switching. Due to the photodoping of grown films, the areas under illumination or that have been illuminated, during this potential step procedure remain while the areas not under illumination or not subject to illumination are stripped away by dissolution.

[00039] Patterning the light via a transparency mask allows for the patterning of regions of photodoped Cu_2O, and therefore the two-dimensional structure of the thin film on the electrode surface. In one embodiment, the conductive interface may be a transparent fluorine-doped tin oxide on glass electrode.

[00040] A number of different methods may be used to create the patterns. In the embodiment shown in Figure 1, pattern 100 is formed on a first surface of substrate 120 while mask 116 is located on an opposingly located second surface. For this embodiment, light source 110 and mask 116 are used to create patterns of light that are transmitted through transparent substrate 120. This creates the illumination patterns that alter the Cu_2O. In other words, the backside of the substrate is illuminated for this embodiment. Patterns may then be created as described above.

[00041] As shown in Figure 3A, pattern 300 may be created from illuminating the front side of the substrate 306. For this embodiment, patterning from the front allows for the use of non-transparent substrates and also allows for the patterning to occur on the growing interface 304. To promote the growth of the Cu_2O pattern, mask 310 needs to be located a spaced distance away from growing surface 304 so as to not block the solution from reaching surface 304. Patterns may then be created as described above.

[00042] In yet another embodiment of the present invention, a projector may be used to create the illumination patterns from either the front side or backside. This would eliminate the need to use mask 116 or 301. Patterns may then be created as described above. In other embodiments, the projection source can be used to produce a time-dependent, two-dimensional illumination pattern (like an image) that changes while the film is grown to add three-dimensional structure to the film. Under constant cathodic electrodeposition potential, changing the illumination patterns, by time, intensity, color of the illumination, or any combination of these

three illumination parameters as a dynamical illumination image creates a three-dimensional, photodoped "black" Cu_2O structure into the thin film. Under the cathodic electrodeposition/anodic dissolution work cycle, this can result into a printed three-dimensional structure of Cu_2O on the electrode surface. In either case, portions of the deposited film can be removed by chemical dissolution or through electrochemical stripping during growth to produce a thin film patterned in three dimensions. This method could be used to grow three-dimensional templates (like stamps or molds), structured electrocatalysts, three-dimensional circuits, metamaterials (nanostructured materials with non-intuitive optical properties, like negative refractive index or generation of strange polarizations), or nanotextured, low-friction tribological surfaces.

[00043] Figures 3A and 3B also show a two-step scheme for the solution-phase light-directed patterning of noble metal surfaces based on the photolithographic properties of Cu_2O for another embodiment of the present invention. As shown in Figure 3A, photolithographic patterning of Cu_2O 300 and 302 on a conductive surface 304 and substrate 306 may be accomplished as described above through the use of a mask and illumination source.

[00044] The patterned film may be fabricated, in a preferred embodiment, with an electrochemical duty cycle of cathodic Cu_2O deposition followed by anodic dissolution. The remaining Cu_2O is the portion of the film that was exposed to light during growth. The steps of depositing, illuminating and dissolution may be repeated.

[00045] The second step of the embodiment is shown in Figure 3B. As shown, this step utilizes the galvanic replacement of Cu_2O 300 and 302 with Au, Ag, or other noble metals 350A-350F that spontaneously form on the surface while oxidizing the Cu_2O back to soluble Cu2+ ions.

[00046] The present invention may be used to fabricate integrated circuits, print interconnections between electrical components, perform three-dimensional patterning of circuits, provide direct write lithography masks, pattern semiconductor structures for photovoltaics or photoelectrochemical cells,

electrocatalyst patterning, controlling the composition of multi-metal electrocatalysts, photodoping Cu2O to form electrodeposited PN junctions for electrical diodes and photovoltaics, microelectrode patterning for dry cell batteries (via low temp oxidation to CuO).

[00047] In still other embodiments, the present invention provides a method to pattern the local doping/chemistry of thin films of cuprous oxide with light. By illuminating cuprous oxide with photon energies above the band gap energy of 2.0eV, the illuminated area of the cuprous oxide thin film is increasingly darkened with increasing intensity during electrodeposition. By stepwise scanning of the electrode potential, the area of the thin film not under illumination can be stripped from the electrode, leaving the remaining illuminated areas on the electrode or conductive surface. This process allows for directly writing copper-based structures on electrodes to either pattern regions of Cu_2O semiconductor or to pattern conductive Cu patterns for circuits. The Cu patterns may then be replaced with one or more noble metals as described above.

[00048] In one application of the the present invention, Cu_2O films were submerged in 5mM NaAuCl4 GRR solution (pH 2.7) for 0 s, 10 s, 1 min, 2 min, and 60 min. The Cu 2p spectra show that the starting Cu_2O surface quickly oxidizes to CuO. Eventually all of the CuO/ Cu_2O dissolves as indicated by the lack of the Cu XPS features after 60min. A Cu_2O film that was air-annealed (400 C for 1 hour) to CuO still showed the CuO XPS features after 60 minutes in the Au solution. The Au 4f spectra show that Au begins to deposit within the first 10 s of exposure and increases intensity. The CuO film shows no Au deposition after 60 minutes.

[00049] Figures 5A and 5B are comparisons of Cu 2p and Au 4f XPS spectra for Cu_2O films submerged in an aqueous buffer (pH 2.7) with 10 s, 1 min and without NaAuCl4. Plain, unexposed Cu_2O is shown for reference. The Cu 2p spectra show that without NaAuCl4 in the solution, the Cu_2O surface maintains its oxidation state through dissolution. The solid-state oxidation to CuO only occurs in the presence of AuCl4(-) reduction.

[00050] Figures 6A and 6B are SEM micrographs of the nanoscale morphology and microstructure of GRR-deposited Au on Cu_2O after a 5-minute exposure.

[00051] Figure 7A illustrates GRR-deposited Au on Cu_2O without illumination as shown in Figure 4A. Figure 7B illustrates GRR-deposited Au on Cu_2O with 455nm LED illumination but without NaAuCl4 in the solution. Figure 7C illustrates GRR-deposited Au on Cu_2O and with 455nm LED illumination and with NaAuCl4 in the solution.

[00052] In yet other embodiments, the present invention provides methods for creating patterns by electrodeposition that are not limited to Cu_2O, but include other materials that may be deposited by electrodeposition. In a preferred method, a film of photoactive material having an electrodeposition polarity that matches its photoactive polarity is deposited in two ways. First by electrodeposited and by the application of light. The light acts as an additional bias which results in additional deposition of material. Thus, in areas of the illumination, the deposition rate of material is greater that in the non-illuminated areas, creating a pattern of areas with more deposited material as compared to the non-illuminated areas.

[00053] In circumstances where the desired pattern is to include areas of deposited material and areas where there is no deposited material, the illumination may be continued during the reversal of the polarity. Reversing the polarity causes dissolution of the deposited material. Non-illuminated areas have a higher rate of dissolution than the illuminated areas since the illumination reverses or retards the magnitude of the reverse polarity. Thus, non-illuminated areas are stripped of deposited material at a higher rate and will have all material removed prior to the removal of all material from the illuminated areas.

[00054] While the foregoing written description enables one of ordinary skill to make and use what is considered presently to be the best mode thereof, those of ordinary skill will understand and appreciate the existence of variations, combinations, and equivalents of the specific embodiment, method, and examples herein. The disclosure should therefore not be limited by the above described

embodiments, methods, and examples, but by all embodiments and methods within the scope and spirit of the disclosure.

WHAT IS CLAIMED IS:

1. A method of creating a patterned film with cuprous oxide and light comprising the steps of:

(a) electrodepositing copper from a solution onto a substrate;

(b) illuminating selected areas of said deposited copper with light having photon energies above the band gap energy of 2.0eV to create selected illuminated sections and non-illuminated sections; and

(c) stripping non-illuminated sections leaving said illuminated sections on the substrate.

2. The method of claim 1 wherein the substrate is a transparent, conductive substrate.

3. The method of claim 1 wherein the substrate is a non-transparent, conductive substrate.

4. The method of claim 1 wherein the pattern is made from Cu_2O having chemically distinct phases.

5. The method of claim 1 wherein the pattern is a thin film having features including sub-millimeter features.

6. The method of claim 1 wherein Cu_2O is galvanically replaced with a noble metal and said Cu_2O is reduced back to soluble Cu2+ ions.

7. The method of claim 9 wherein said noble metal is Au.

8. The method of claim 9 wherein said noble metal is Ag.

9. The method of claim 1 wherein stripping occurs after illumination.

10. The method of claim 1 wherein stripping occurs during illumination.

11. The method of claim 1 wherein stripping occurs in-between illumination.

12. The method of claim 1 wherein a projector is used to illuminate selected areas of said deposited copper.

13. The method of claim 1 wherein a light source and a mask located a spaced distance from said deposited copper are used to illuminate selected areas of said deposited copper.

14. The method of claim 13 wherein the surface of the substrate on which the copper is deposited is illuminated.

15. The method of claim 1 wherein a light source and a mask located on a transparent substrate are used to illuminate selected areas of said deposited copper.

16. The method of claim 15 wherein an opposingly located surface of the substrate on which the copper is deposited is illuminated.

17. The method of claim 1 wherein steps (a)-(c) are repeated.

18. A method of creating a pattern on a substrate using electrodeposition and light comprising the steps of:

on selected areas of said substrate, depositing material by electrodeposition and by illumination to create a deposition rate of material that is greater than in the non-illuminated areas; and

reversing the polarity while maintaining the illumination of said selected areas to cause said non-illuminated areas to have a higher rate of dissolution than said selected areas.

19. The method of claim 18 wherein said deposited material is copper.

20. The method of claim 18 wherein said illumination is changed by time to create three-dimensional patterns.

21. The method of claim 18 wherein said illumination is changed by intensity to create three-dimensional patterns.

22. The method of claim 18 wherein said illumination is changed by color of the illumination to create three-dimensional patterns.

23. The method of claim 18 wherein said illumination is changed by a combination of color of the illumination, time or intensity to create three-dimensional patterns.

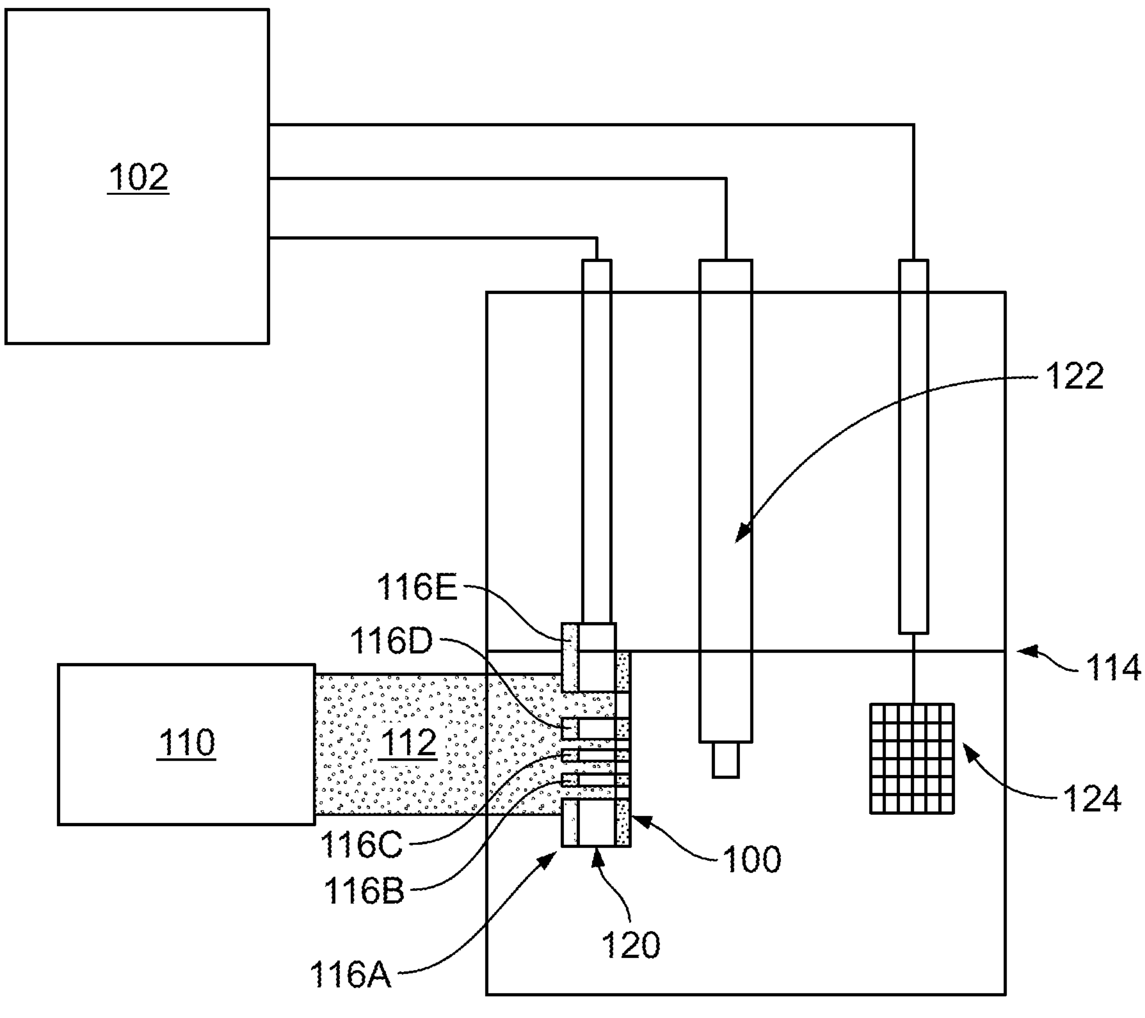

FIG. 1

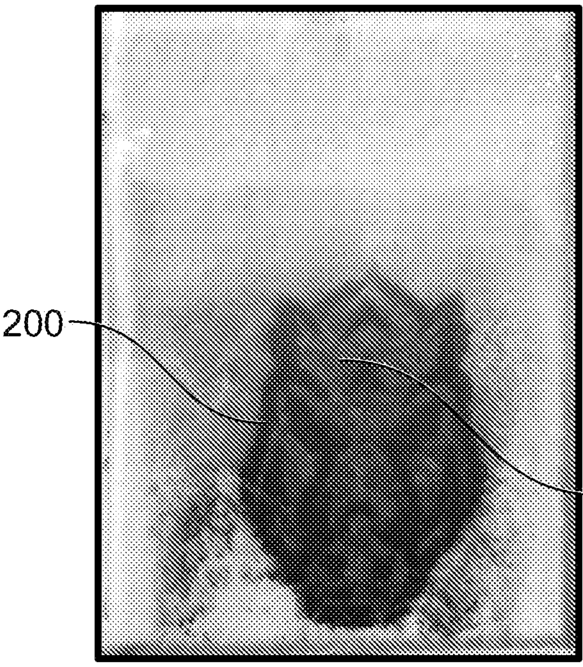

FIG. 2A

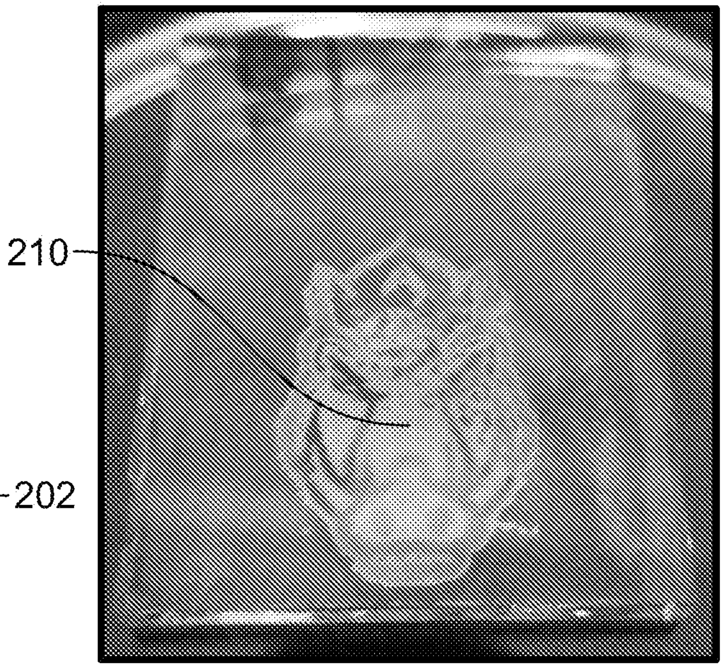

FIG. 2B

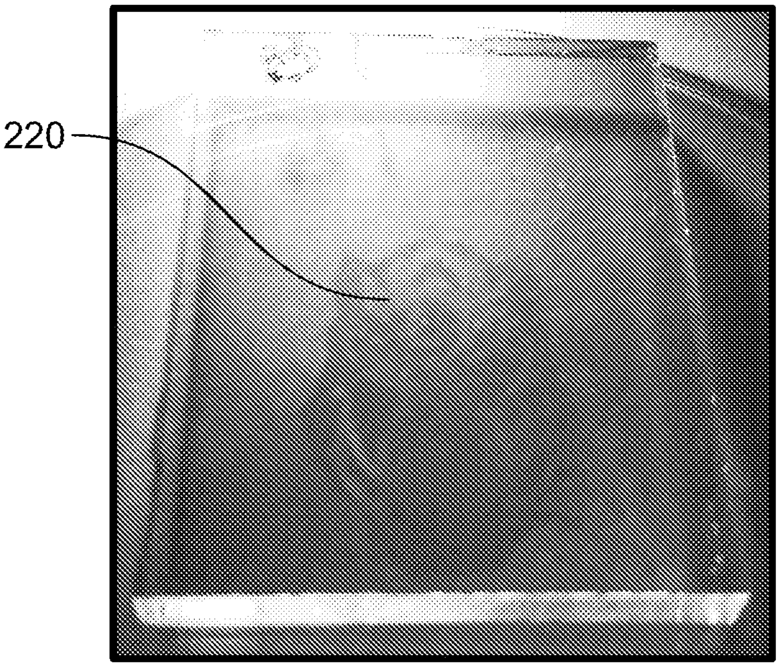

FIG. 2C

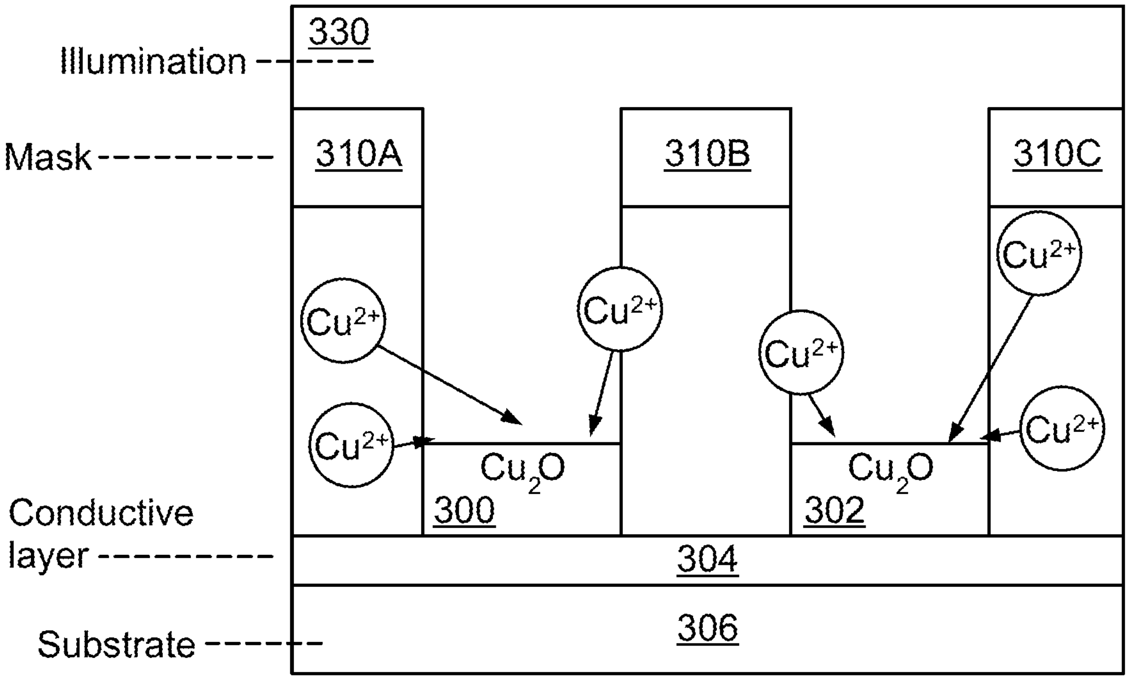
330
Illumination
Mask
310A
310B
310C
Cu^{2+}
Cu^{2+}
Cu^{2+}
Cu^{2+}
Cu^{2+}
Cu^{2+}
Cu_2O
300
Cu_2O
302
Conductive layer
304
Substrate
306

FIG. 3A

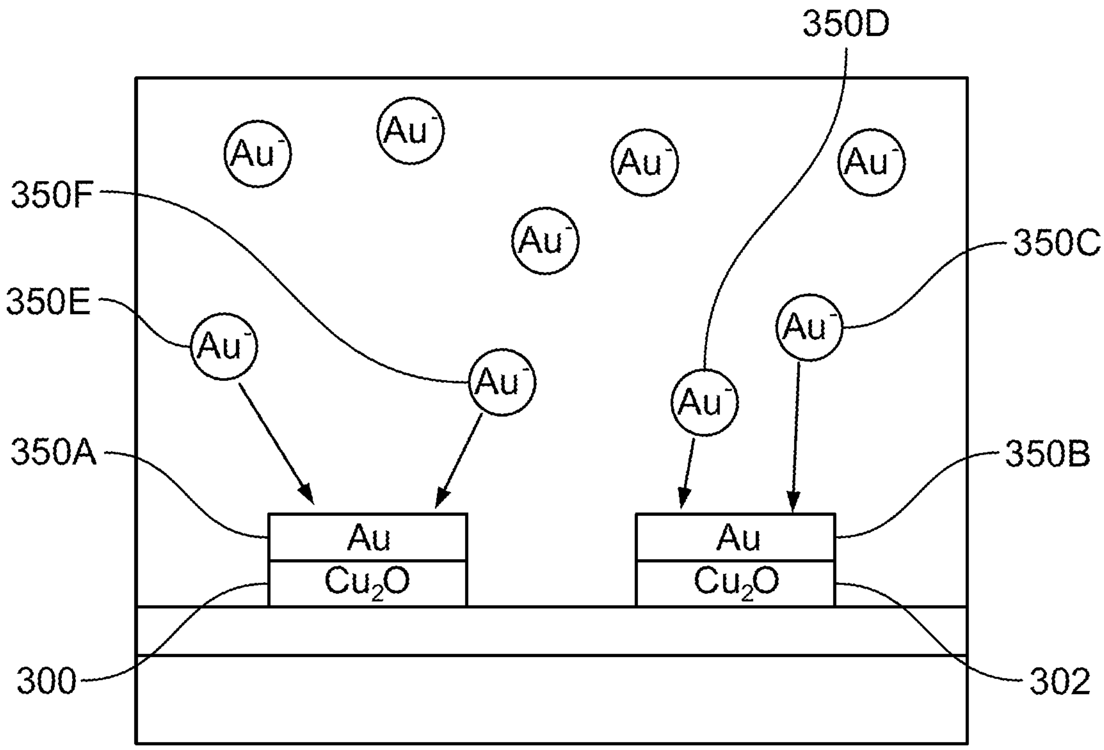
350D
Au^-
350F
350C
350E
350A
350B
Au
Cu_2O
Au
Cu_2O
300
302

FIG. 3B

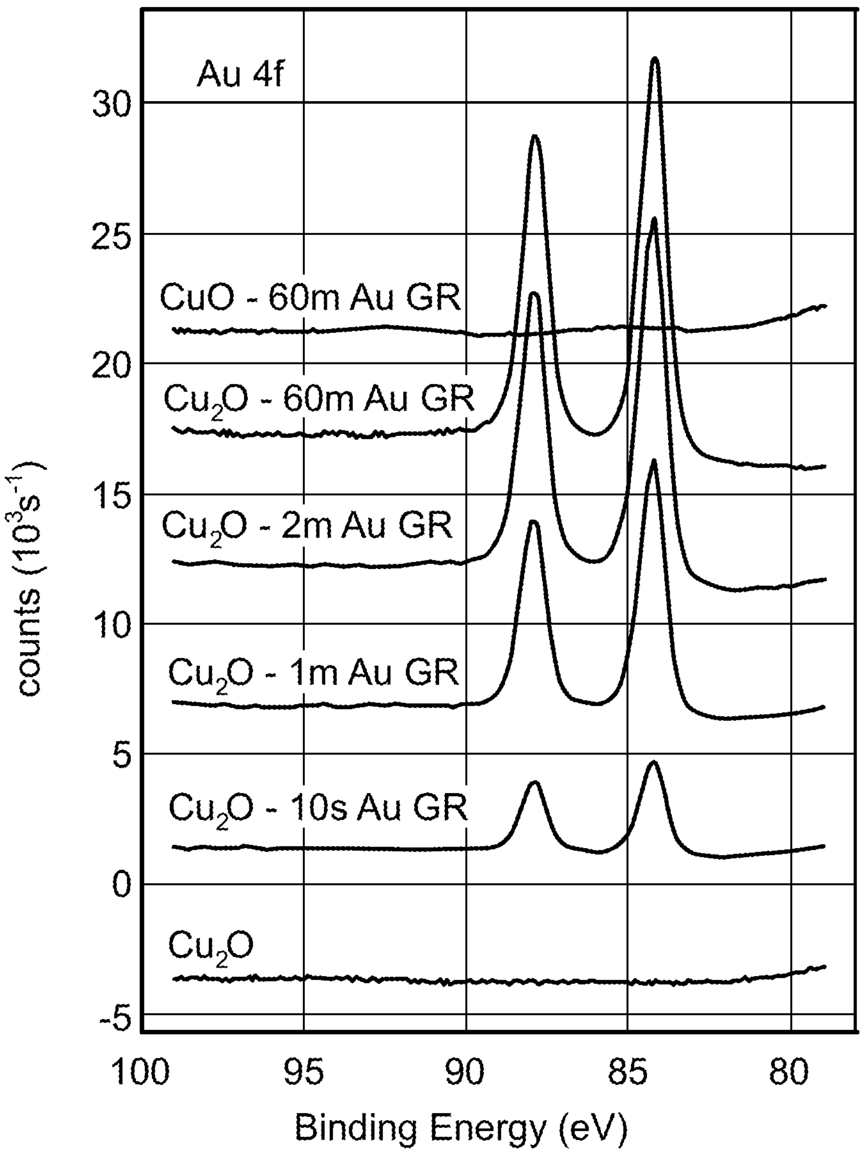
Au 4f
CuO - 60m Au GR
Cu_2O - 60m Au GR
Cu_2O - 2m Au GR
Cu_2O - 1m Au GR
Cu_2O - 10s Au GR
Cu_2O
counts (10^3s^{-1})
Binding Energy (eV)
30
25
20
15
10
5
0
-5
100
95
90
85
80

FIG. 4A

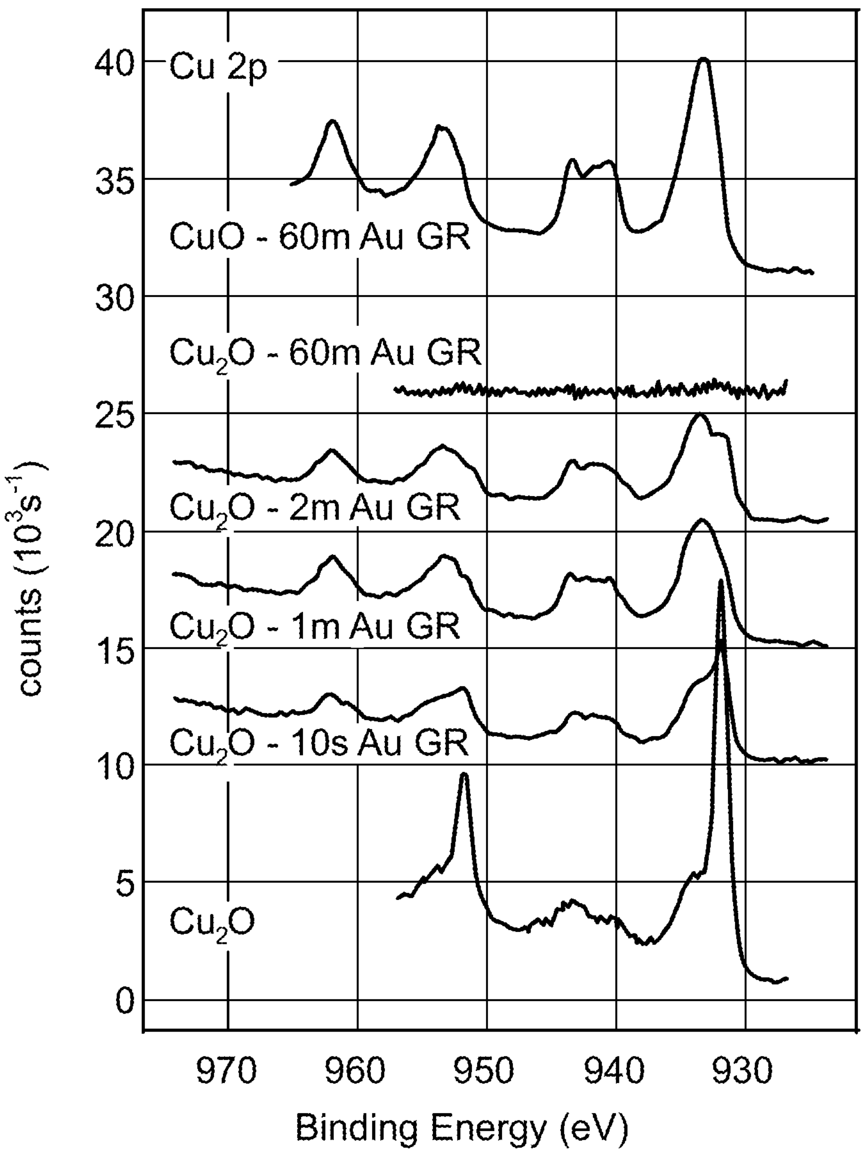
Cu 2p
CuO - 60m Au GR
Cu_2O - 60m Au GR
Cu_2O - 2m Au GR
Cu_2O - 1m Au GR
Cu_2O - 10s Au GR
Cu_2O
counts (10^3s^{-1})
Binding Energy (eV)
40
35
30
25
20
15
10
5
0
970
960
950
940
930

FIG. 4B

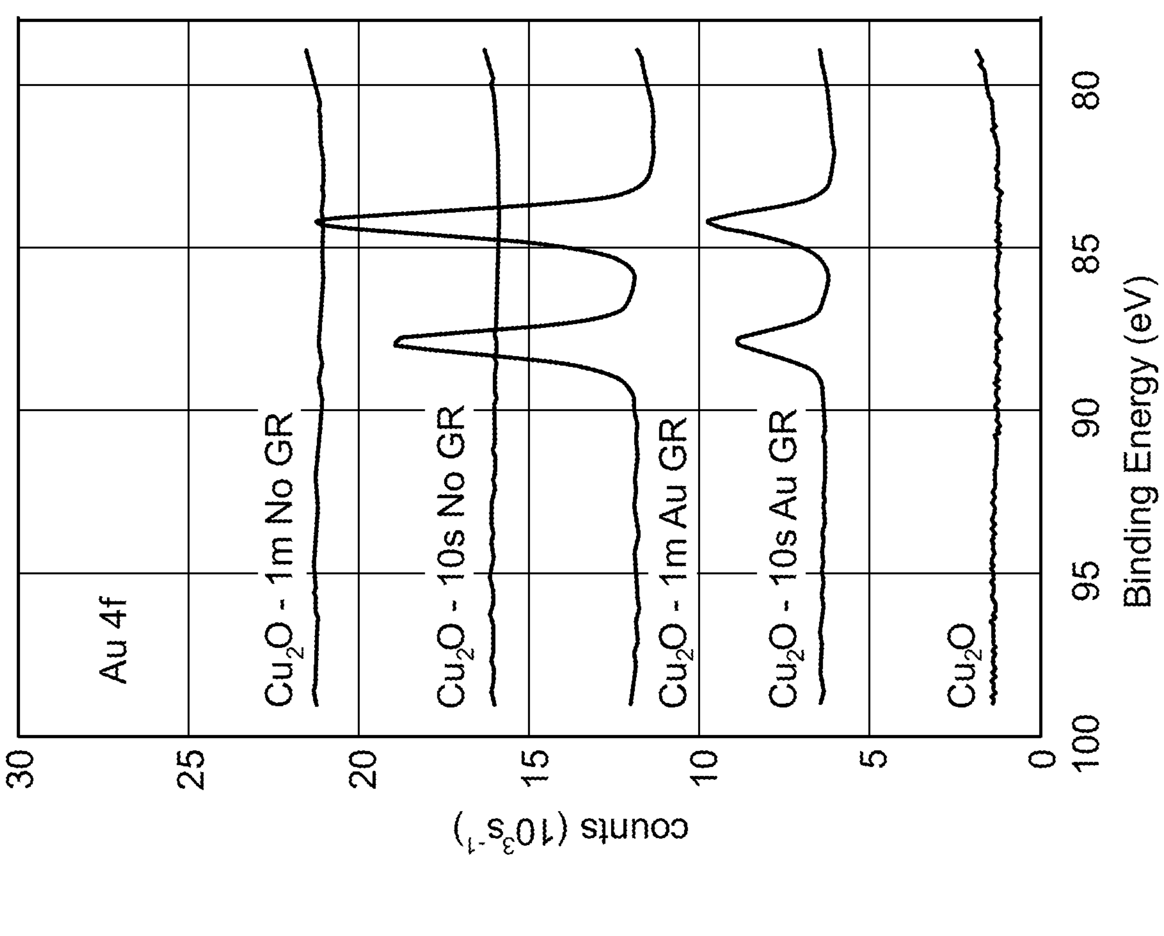
Au 4f
Cu2O - 1m No GR
Cu2O - 10s No GR
Cu2O - 1m Au GR
Cu2O - 10s Au GR
Cu2O
counts (10³s⁻¹)
Binding Energy (eV)
0
5
10
15
20
25
30
100
95
90
85
80

FIG. 5A

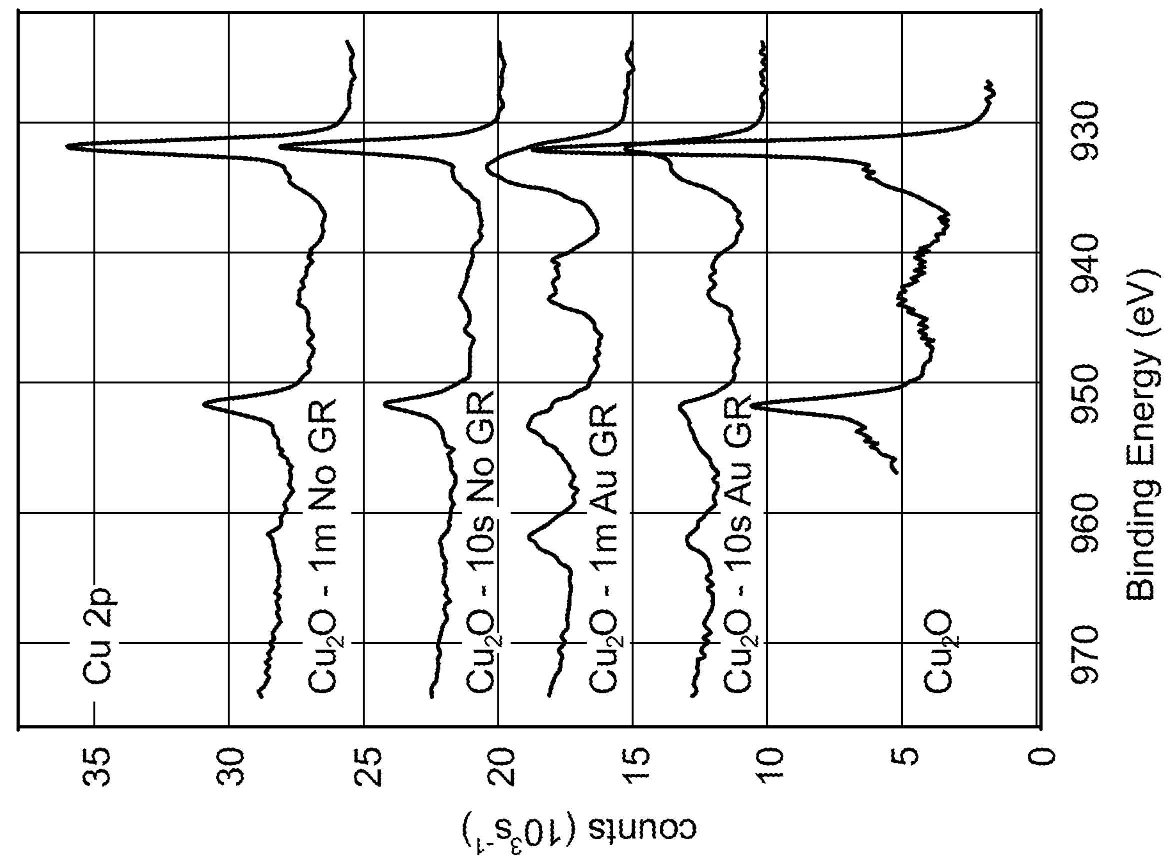
Cu 2p
Cu2O - 1m No GR
Cu2O - 10s No GR
Cu2O - 1m Au GR
Cu2O - 10s Au GR
Cu2O
counts (10³s⁻¹)
Binding Energy (eV)
0
5
10
15
20
25
30
35
970
960
950
940
930

FIG. 5B

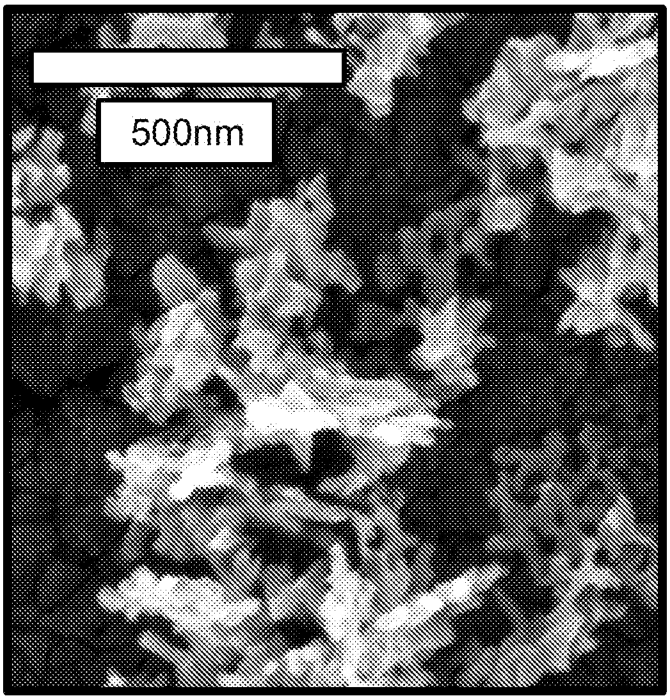

FIG. 6A

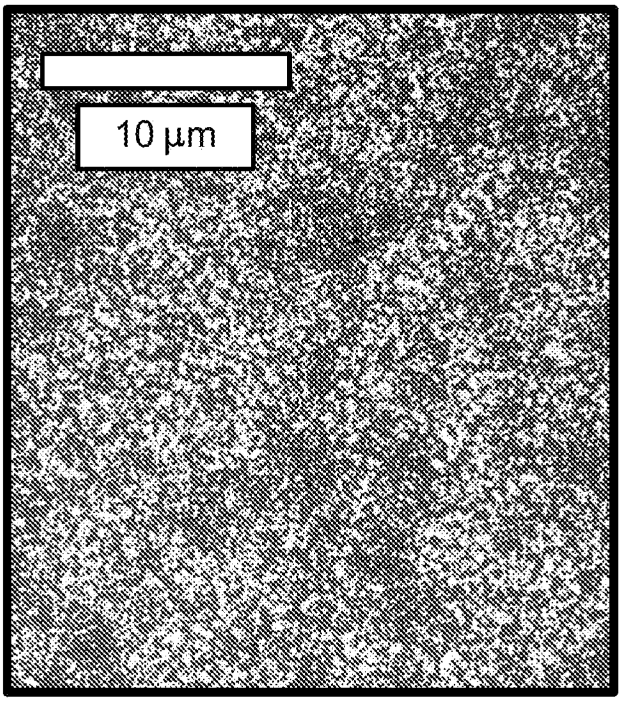

FIG. 6B

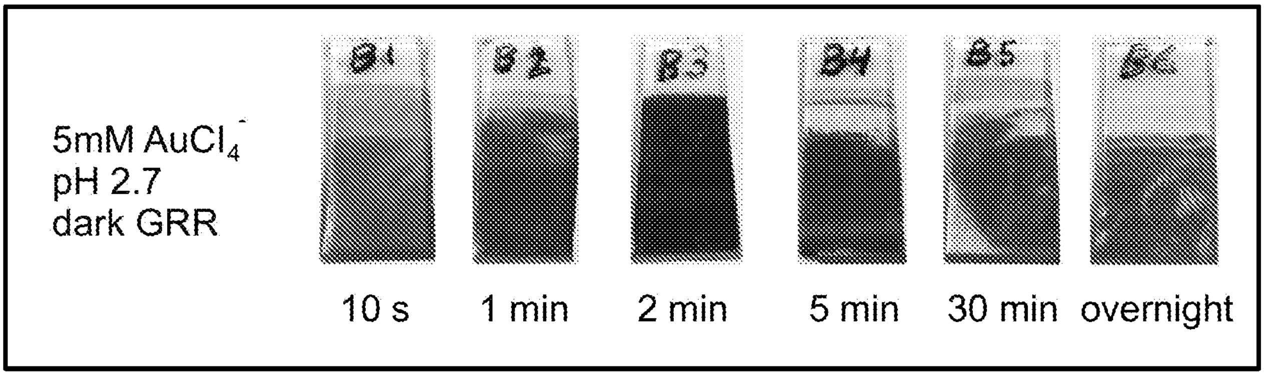

FIG. 7A

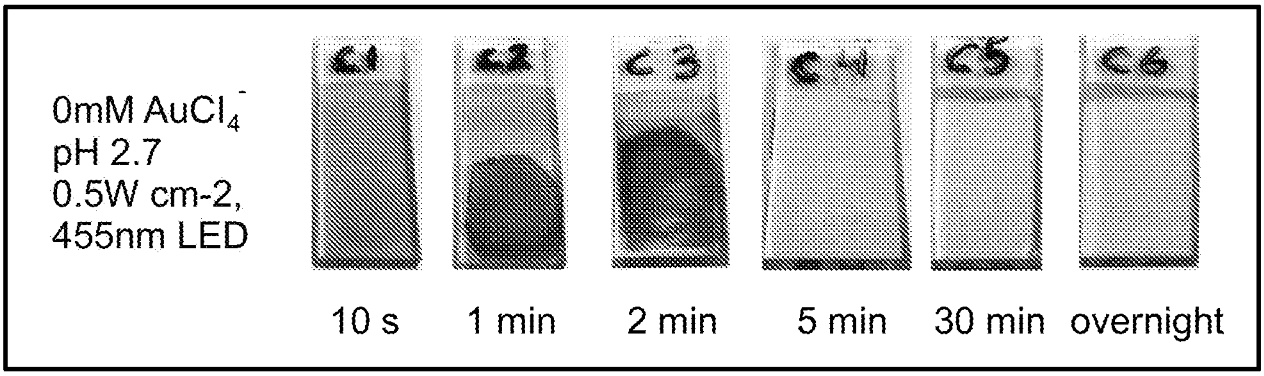

FIG. 7B

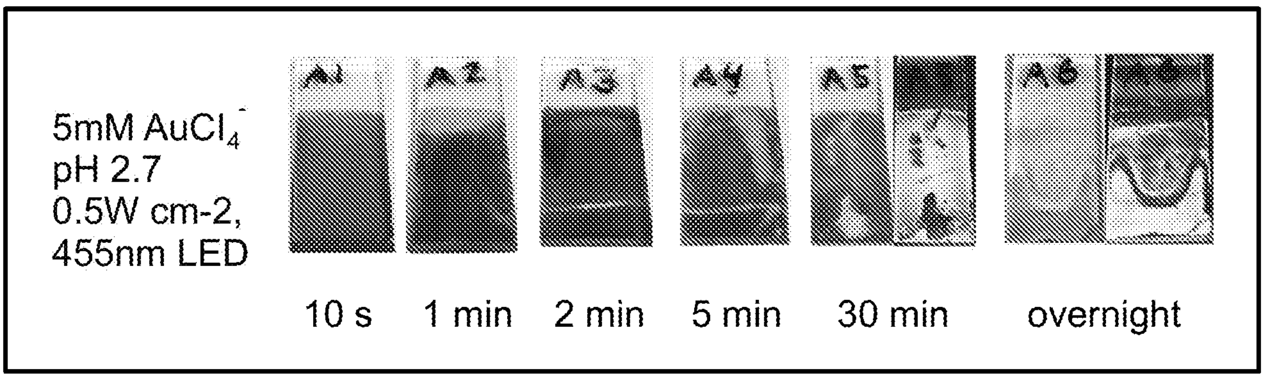

FIG. 7C

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2017/049187

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C25D 7/12; C25D 5/00; C25D 5/02; C25D 17/00; H01L 21/3065 (2017.01)
CPC - C25D 7/12; C25D 5/00; C25D 5/02; C25D 17/00; H01L 21/3065 (2017.08)

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
See Search History document

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC - 204/242; 205/91; 205/123; 438/735 (keyword delimited)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
See Search History document

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 8,795,502 B2 (COTTE et al) 05 August 2014 (05.08.2014) entire document	1-17
Y	US 2013/0309873 A1 (RUZIC et al) 21 November 2013 (21.11.2013) entire document	1-17
Y	US 2012/0175147 A1 (NAKAKO et al) 12 July 2012 (12.07.2012) entire document	1-17
Y	US 2015/0259816 A1 (MACDERMID ACUMEN, INC) 17 September 2015 (17.09.2015) entire document	2
Y	WO 2016/020759 A1 (KING ABDULLAH UNIVERSITY OF SCIENCE AND TECHNOLOGY) 11 February 2016 (11.02.2016) entire document	6-8
Y	US 2006/0057474 A1 (KOIKE et al) 16 March 2006 (16.03.2006) entire document	15, 16
A	US 2004/0057688 A1 (AKUTSU et al) 25 March 2004 (25.03.2004) entire document	1-17
A	US 2011/0011745 A1 (JI et al) 20 January 2011 (20.01.2011) entire document	1-17
A	US 5,595,637 A (TENCH et al) 21 January 1997 (21.01.1997) entire document	1-17

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
30 November 2017	22 DEC 2017

Name and mailing address of the ISA/US	Authorized officer
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, VA 22313-1450 Facsimile No. 571-273-8300	Blaine R. Copenheaver PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US2017/049187

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

See extra sheet(s).

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-17

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

Continued from Box No. III Observations where unity of invention is lacking

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I, claims 1-17, drawn to a method of creating a patterned film with cuprous oxide and light.
Group II, claims 18-23, drawn to a method of creating a pattern on a substrate using electrodeposition and light.

The inventions listed as Groups I-II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: the special technical feature of the Group I invention: illuminating selected areas of said deposited copper with light having photon energies above the band gap energy of 2.0eV to create selected illuminated sections and non-illuminated sections; and (c) stripping non-illuminated sections leaving said illuminated sections on the substrate as claimed therein is not present in the invention of Group II. The special technical feature of the Group II invention: to create a deposition rate of material that is greater than in the non-illuminated areas; and reversing the polarity while maintaining the illumination of said selected areas to cause said non-illuminated areas to have a higher rate of dissolution than said selected areas as claimed therein is not present in the invention of Group I.

Groups I and II lack unity of invention because even though the inventions of these groups require the technical feature of a method of creating a pattern on a substrate using electrodeposition and light comprising the steps of: on selected areas of said substrate, depositing material by electrodeposition and by illumination, this technical feature is not a special technical feature as it does not make a contribution over the prior art.

Specifically, US 2004/0057688 A1 (AKUTSU et al.) 25 March 2004 (25.03.2004) teaches a method of creating a pattern on a substrate using electrodeposition and light comprising the steps of: on selected areas of said substrate, depositing material by electrodeposition and by illumination (paras. 0184, 0188).

Since none of the special technical features of the Group I or II inventions are found in more than one of the inventions, unity of invention is lacking.