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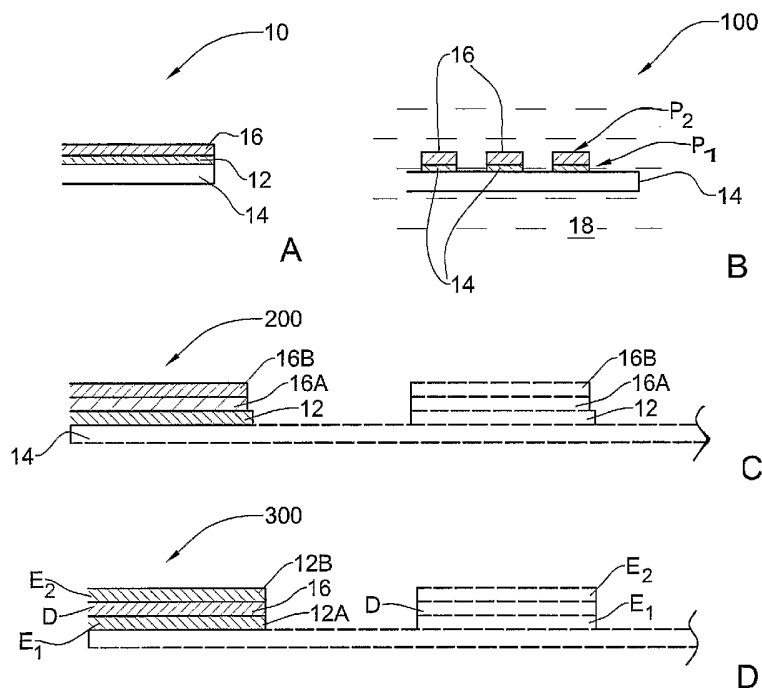
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(54) Title: ELECTROCHEMICAL DEPOSITION PROCESS AND DEVICES OBTAINED BY SUCH PROCESS



(57) Abstract: The present invention provides an electrochemical method for depositing a thin film comprising metal oxides or silicon oxides on a conductive surface placed on a non-conductive substrate by electrodeposition of sol-gel precursors on the conductive surface selectively. The sol-gel precursors may further comprise various dopants thereby patterning the conductive layer.



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ELECTROCHEMICAL DEPOSITION PROCESS AND DEVICES OBTAINED BY SUCH PROCESS

FIELD OF THE INVENTION

This invention relates to a method for the electrochemical deposition and devices obtained by such process.

BACKGROUND OF THE INVENTION

5 Specific coating of structures displayed on a substrate becomes more and more complex as the structure to be coated and the substrate are miniaturized. Selective coating of complex shapes situated on a 2- or 3-dimensional surface employs techniques such as chemical masks (<http://www.Intel.com>) and electrophoretic methods (Gal-Or, L., Liubovich, S., Haber, S. (1992) *J. Electrochem. Soc.* **139**, 1078-1081). These two widely known techniques are
10 frequently, time consuming, inefficient and more so may be inaccurate or damage the substrate. Chemical masks utilize hazardous materials and resolution is not sufficient. Furthermore, the etching is not selective enough and may proceed further or deeper than originally intended. Electrophoretic methods
15 employ micrometric-size particles which are not suitable for sub-micrometric-size shapes. Furthermore, the coated products have rather rough coating. Another drawback of electrophoretic methods is the use of high voltage which may damage the sample undergoing a coating procedure. These drawbacks worsen as the geometry of the structure becomes more complex and are miniaturized.

20 Using a sol-gel process for coating metals with metal alkoxides is known (Lu, Y. et al. (1997) *Nature* **389**, 364) and a variety of film formation procedures were developed. Utilizing an electrochemical approach for film formation has been limited to electrophoretic deposition of colloidal metal hydroxide particles (Nishimori, H. et al. (1996) *J. Sol Gel Sci. Technology* (1996) **7**, 211),
25 electrodeposition of alkoxysilane (Leventis, N. & Chen, M (1997) *Chem. Mater.*

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9, 2621) and electrooxidation of metals (Lee, G.R. & Crayston, J.A. (1996) *J. Mater. Chem.* **6**, 187). Recently, the inventors of the present invention have developed a method for coating of a conducting material by electrodeposition of a sol gel film of silicon oxide originating from methyltrimethoxysilane
5 (Shacham, R, et al. (1999) *Adv. Mater.* **11**, 384-388). The mechanism of the electrochemical sol-gel coating described in this reference involves the alteration of the local pH next to the conducting surface resulting in an enhancement of the deposition of the desired coating film specifically on the desired surface. This technique is suitable for sol-gel coating of flat surfaces utilizing a basic pH above
10 8.2 by introducing a basic material.

SUMMARY OF THE INVENTION

There is a need in the art to facilitate formation of a conductive pattern on a non-conductive substrate, as well as selective processing of a conductive surface that might be located adjacent to a non-conductive surface. A classical
15 problem in the thin-films world (manufacture of patterned structures such as semiconductor devices) is associated with such methods as dip-coating, spin-coating, spraying without masks, which can not be used for patterning complex structures, because conventional patterning techniques do not differentiate between conducting vs. non-conducting areas, but rather utilize coating of the
20 entire surface followed by etching in accordance to a pattern to be obtained.

The present invention is directed to an electrochemical method for depositing a thin film comprising metal- or transition metal- oxides or silicon oxides on a conductive surface comprising:

- (i) providing a conductive surface;
- 25 (ii) immersing the conducting surface in a solution comprising sol-gel precursor which is comprised of monomers or prepolymers comprising metal, transition metal or Si compounds; alcohol; a determined amount of water and an inert soluble salt;

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(iii) carrying out an electrodeposition process by applying substantially low voltages to create negative or positive potential for a predetermined period of time to induce sol-gel reaction at the conductive surface, thereby obtaining conductive surface coated with a thin film having desired thickness and comprising oxides of silicon and/or metal and/or transition metal formed by said sol-gel reaction

The novel low-voltage electrochemical technique is capable of differentiating between conducting and non conducting surfaces. The technique consists of subjecting a non-conductive substrate, carrying a conductive region or patterned with a plurality of spaced-apart conductive regions, to an electrochemical potential while immersed in a solution, thus selectively coating only the conductive region(s) while not coating the non-conductive surface of the substrate. Accordingly, conductive material present on a non-conductive material can selectively be coated with a thin film, where the thickness of the film is controlled. The selective coating is done by an electrochemically induced sol-gel process.

Thus the present invention is further directed to a method according to claim 1 for depositing the thin film on the conductive surface carried by a non-conductive substrate, the method comprising:

- (i) providing a non-conductive substrate carrying a pattern formed by at least one conductive surface region on said substrate;
- (ii) immersing said substrate in a solution comprising sol-gel precursors monomers or pre-polymers comprising metal, transition metal or Si compounds; an alcohol; a determined amount of water and an inert soluble salt;
- (iii) carrying out electrodeposition process by applying substantially low voltages to create negative or positive potential for a determined period of time to induce selective sol-gel reaction occurring at the conductive surface to produce sol-gel thin film of a desired thickness comprising oxides of silicon, metal or transition metal,

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thereby obtaining the pattern on the non-conductive substrate formed by the at least one conductive surface region coated with the sol-gel thin film surrounded by non-conductive regions of the substrate.

The sol-gel precursor is selected from metal, transition metal or silicon alkoxide monomers or ester monomers or monomers of the formula $M(R)_n(P)_m$, wherein M is a metallic or semi metallic element or Si, R is a hydrolyzable substituent, n is an integer from 1 to 4, P is a non polymerizable substituent and m is an integer from 0 to 3, or partially hydrolyzed and partially condensed polymer thereof, or any mixture thereof. More specifically, the sol-gel metal and/or silicon precursor is in the form of $R'_m-X-(OR)_n$, and the alcohol is ROH, wherein X is a metal, transition metal or silicon or mixtures thereof, R' is an alkyl or aryl optionally substituted with an amine or thiol, $n+m = 4$, and R is a C_{1-3} -alkyl. The sol-gel metal and transition metal are selected from zirconia, titania, alumina, iron, vanadium, cobalt nickel, tungsten and combinations thereof. Thus the coating material is a metal oxide derived from the respective metal alkoxide. The sol-gel precursors may also be pre-polymers, being short polymers composed of a few units of monomers.

According to the present invention, the thickness of the formed film is controlled through duration of the sol-gel reaction and/or applied voltage and may have a thickness of from a few monolayers to about a micron, preferably from about 10nm to about 1000nm. The duration of the applied potential is preferably less than one hour, more preferably from about 5 minutes to about 45 minutes.

The present invention can be used for example in the manufacture of capacitors by fabricating dielectric spacer between the capacitor plates utilizing the selective coating of the present invention.

Another possible application of the present invention is the manufacture of integrated electronic devices, such as optical devices utilizing a stack of materials with different optical properties. This is due to the fact that the technique of the present invention provides for selectively coating with a material

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of a desired refractive index, and moreover provides for varying the refractive index during the coating procedure.

The present invention can further be used in the manufacture of flat panel displays, by selectively coating by electrodeposition cathode elements (tips) that
5 are typically arranged in a spaced-apart relationship on a non-conductive substrate, with a photosensitive material. Since the technique of the present invention is not limited to the critical dimensions of the conventional lithography, and keeping in mind that growing of nanotip-cathodes is already known, the selective coating of the present invention provides for reducing the
10 pixel size into a nanoscale. The present invention can also be used for manufacturing the pixel array of a photodetector.

The technique of the present invention can also be used in the manufacture of printed circuit boards. It is known (for example from WO 03/018871) that a pattern formed by spaced-apart conductive regions on a non-conductive structure
15 can be obtained by irradiating with a focused laser beam the spaced-apart regions of a substrate comprising one or more thermally degradable compounds, thus resulting in local deposition of carbon within said regions. By selectively coating only the conductive carbon-containing regions with a material of an electrical conductivity higher than that of carbon (which by itself might not provide
20 sufficient conductivity for an electronic circuit), the pattern of desired conductors on the non-conductive substrate can be created.

The selective coating process of the present invention may further be employed to the manufacture of materials having spatially non-homogenous microstructures and properties by coating spatially different layers. Such blended
25 layers of coatings form a functionalized graded material where the coating consists of at least two layers where each of them has a different ratio of metal to metal oxide in the layer. This is due to the fact that the technique of the present invention enables to timely vary the electrochemically negative or positive potential during the coating process, where the variation of potential results in a
30 different ratio of metal to metal oxide in the coated layer.

BRIEF DESCRIPTION OF THE DRAWINGS

In order to understand the invention and to see how it may be carried out in practice, a preferred embodiment will now be described, by way of non-limiting example only, with reference to the accompanying drawings, in which:

5 **Figs. 1A-1D** illustrate in a schematic manner various possible devices obtainable by the novel electrochemical deposition of the present invention.

Fig. 2. shows a High Resolution Scanning Electron Microscope (HR-SEM) image of a gold mesh coated with TiO_2 . (a) bare gold mesh; (b) TiO_2 coating by dip-coating; (c) TiO_2 coating by electrodeposition.

10 **Fig. 3** shows an Electron Diffraction Spectroscopy (EDS) map of a gold mesh coated with TiO_2 . (a) bare gold mesh (only Au seen); (b) & (c) TiO_2 coating by dip-coating (Au and Ti, are shown, respectively); (d) & (e) TiO_2 coating by electrodeposition (Au and Ti, are shown, respectively).

Fig. 4 shows the selective coating of a conductive aluminum pattern
15 sputtered on silicone with ZrO_2 . (a) HR-SEM image of a sputtered conductive pattern of Al on Si, (b-d) EDS element-mapping of sample coated by ZrO_2 upon dip-coating (seen are Al, Si and Zr, respectively), (e-g) EDS element-mapping of sample coated by ZrO_2 upon applying -1.2 V for 30 min (seen are Al, Si and Zr, respectively). The bar is 10 μm .

20 **Fig. 5** shows the selective coating of a conductive aluminum pattern sputtered on silicone with TiO_2 . (a) HR-SEM image of sputtered Al on Si coated by TiO_2 upon dip-coating, (b-d) EDS element-mapping of sample coated by TiO_2 upon dip-coating (seen are Al, Si and Ti, respectively), (e) HR-SEM image of sputtered Al on Si coated by TiO_2 upon applying -1.4 V for 15 min, (f-h) EDS
25 element-mapping of sample coated by TiO_2 upon applying -1.4 V for 15 min (seen are Al, Si and Ti, respectively).

Fig. 6 shows atomic force microscopy (AFM) images of 5X5 μm samples before and after coating with ZrO_2 . (a) bare indium tin oxide (ITO) plate, the roughness value is 7.622 nm and the z-axis scale is 80 nm; (b) dip-coated ITO
30 plate, the roughness value is 0.615 nm and the z-axis scale is 20 nm; (c)

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electrodeposition applying -0.9V for 30 minutes, the roughness value is 0.568 nm and the z-axis scale is 20 nm; (d) electrodeposition applying -1.4V for 30 minutes, the roughness value is 0.522 nm and the z-axis scale is 20 nm.

Fig. 7 shows the effect of added water on the thickness of the electrodeposited ZrO_2 films after applying a voltage (a) -1.2 V and (b) +2.5 V.

Fig. 8 shows the rate of ZrO_2 film buildup on ITO surface applying a voltage of -1.2 V (open circles) or +2.5 V (filled circles).

Fig. 9 shows the initial current densities and current decay profile as a function of the initially applied negative potential on ITO (a-d) and gold (e) electrodes; (a) -1.0 V (b) -1.2 V; (c) -1.4 V; (d) -1.5 V; and (e) -1.4 V.

Fig. 10 shows the chemical reactions occurring during the electrochemical process of the invention employing Zr(OR)_4 as the sol-gel precursor. Applying either a negative or positive potential produces OH^- or H^+ species, respectively, which in turn cause the formation of the desired ZrO_2 (Zr-O-Zr sol-gel film) on the conducted surface serving as one of the electrodes.

DETAILED DESCRIPTION OF THE INVENTION

The present invention provides for a novel process of electrochemical deposition, which allows for patterning a patterned surface by electrochemical pattern recognition. **Figs. 1A-1D** schematically illustrate various devices obtainable by the novel electrochemical deposition. To facilitate understanding, the same reference numbers are used for identifying components that are common in all the examples.

Fig. 1A shows a device **10** formed by a conductive structure (surface) **12** situated on a non-conducting substrate **14** and coated with a thin film **16** resulting from an electrochemically induced sol-gel process where a low-voltage is applied for a predetermined time period. This time period defines the thickness of the film. The substrate **14** with the conductive surface **12** thereon was immersed in a solution including sol-gel precursor monomers, including metal, transition metal

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or Si compounds, alcohol, a determined amount of water and an inert soluble salt; and then an electrodeposition process was carried out by applying substantially low voltages (substantially not exceeding a few voltages in absolute values) to create negative or positive potential during the predetermined period of
5 time to thereby induce a sol-gel reaction at the conductive surface **12**. This results in the formation of the thin film **16** on the surface **12** with a desired thickness of the film. The film **16** includes oxides of silicon and/or metal and/or transition metal formed in the sol-gel reaction.

The conductive surface **12** is any conductive material on the substrate **14**
10 having dimensionality such as thickness and a minimal surface area. The conductive surface may be planar (2-dimensional structure) or curved (3-dimensional structure).

Fig. 1B illustrates a device **100** in the form of a patterned structure, such as a printed circuit board, display device (pixel array defined by the
15 cathode/anode array, etc). The device **100** includes a electrically non-conductive substrate **14** having a pattern **P₁** on its surface formed by an array of electrically conductive regions, generally at **12**, and a pattern **P₂** formed by the same array of thin film regions, generally at **16**, each on top of a corresponding one of the regions **12**. The thin film regions resulted from the selective electro-deposition
20 carried out when the substrate with pattern **P₁** is immersed in a solution **18** (as described above).

Fig. 1C shows a device **200** including an electrically conductive layer **12**, which may or may not be carried by a non-conductive substrate **14** (shown in the figured in dashed lines as its provisional is optional); and at least two thin films
25 (two such films **16A** and **16B** in the present example) stacked on the conductive layer **12**. The films are obtained by immersing the conductive layer **12** in a solution **18** (as described above) and carrying out an electro-deposition process with timely varying value of the applied voltage (low voltage) and possibly also varying dopants to sequentially cause the formation of the thin films **16A** and
30 **16B**. Such a varying electro-deposition process provides for the formation of

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adjacent films with different electrical (conductivity), mechanical, and/or optical (refractive index, luminescence, etc.) properties. As shown in the figure in dashed lines, the device may be an array of spaced-apart stacks, each formed by the conductive layer **12** with two or more thin films **16A**, **16B** thereon, all carried by the non-conductive substrate **14**.

Fig. 1D illustrates a device **300** configured as a capacitor or an array of capacitors, each formed by two electrodes **E₁** and **E₂** spaced by a dielectric spacer **D**. Here, an electrically conductive layer **12** is formed either as a continuous layer or as a patterned layer (spaced-apart regions on a substrate **14**), presenting a single electrode **E₁** or an array of such electrodes. Then the conductive layer (or a patterned conductive layer on a non-conductive substrate) is immersed in a solution **18** prepared to enable formation of a thin film dielectric film **16** (presenting a dielectric spacer **D**) as a result of electro-deposition using appropriate negative or positive voltage (vs. the reference voltage). Then the second electrode **E₂** (or an array of such electrodes) is deposited on the dielectric layer (or dielectric layer regions).

It is important to note that employing the process of the invention is facile and does not require a mask for the patterning purposes. The present invention utilizes low voltages (e.g., -2.0 V to + 2.6 V), compared with a voltage up to 50V in electrophoretic processes. In addition, comparing the invention to the electrophoretic processes which require that the deposited coating is made of small particles made of various monomers, the electrochemical process of the invention utilizes the direct use of monomers, thus saving the step of particles formation. The process of the present invention is a controlled process with regards to the specificity of the coating as well as the thickness of the applied coating.

The present invention provides for an electrochemical process of coating of a conducting surface which may be either a reduction or an oxidation process. Hence the present invention provides coating of a conducting surface at both acidic and basic conditions where the acidic and basic conditions are formed as a

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result of the electrochemical process (formation of either H^+ or OH^- species in solution) and therefore does not require balancing of the solution to a preplanned pH. Conducting the process at a negative potential creates basic conditions (formation of OH^- species) where conducting the reaction at a positive potential
5 creates acidic conditions (formation of H^+ species). The process of sol-gel coating via an electrochemical mechanism of curved surfaces or surfaces having a surface relief is not simple. Such complex patterns (surface relieves) may include holes, steps, kinks which are present on the surface. The technique of the present invention overcomes typical problems in coating of metal grids, porous
10 objects, and inner surfaces of tubes, associated with effects of diffusion, fluidity and surface tension. These effects require careful control of the applied potential in order to obtain a controlled process with regards to specificity of coating and thickness of the coating film. Furthermore, the present invention demonstrates that the coating material may be single silicon or metal oxide coating or a
15 combination of the two or more including a combination of two or more metal oxides. Metals employed in sol-gel processes are either metals or transition metals, hence according to the present invention a layer comprising any mixture of the three components: silicon, metal and transition metal may easily be obtained. The precursors of the sol-gel coating are compounds of the general
20 formula $M(R)_n(P)_m$ in the form of a monomer or in the form of a pre-polymer. M represents a metallic or semi metallic element or Si. Any metal or transition metal may be used where non limiting examples of metals and transition metal elements are zirconium, aluminum, titanium, iron, tungsten, nickel, vanadium or cobalt. R is a hydrolyzable substituents, n is an integer from 1 to 4. P is a non
25 polymerizable substituent and m is an integer from 0 to 3. One may use partially hydrolyzed or partially condensed polymer formed from the $M(R)_n(P)_m$ where the polymer may be a homopolymer (single M) or copolymer (different M). The R and P may also vary with the same M. Non limiting examples of non polymerizable substituents are alkyl, amine, alkylamine or aryl moieties which
30 may be substituted with thiol or amine. More specifically, the sol-gel precursors

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used are in the form of $R'_m-X-(OR)_n$, wherein X is a metal, transition metal or silicon, R' is an alkyl or aryl optionally substituted with amine or thiol, $n+m = 4$, and R is a C_{1-3} -alkyl, preferably methyl or ethyl. The reaction requires the presence of an alcohol and an inert soluble salt. The alcohol is a C_1 - C_4 alcohol preferably, methanol, ethanol, propanol, isopropanol or butanol. Non limiting examples of inert soluble salts are salts of alkali metals, preferably of Na, K and Li such as NaCl, NaBr, KCl, KBr, $LiClO_4$, KNO_3 , KBF_4 and the like.

As a result of the electrochemical process the sol-gel precursor form a metal oxide coating on the conducting surface. The coated metal oxide or combinations of metal oxides may be materials having different dielectric constants thus forming a surface having a controllable and variable dielectric constant from low-K and up. Different sol-gel monomers have different chemical and physical properties enabling the formation of a tailored made surface. Non limiting examples may be water hydrophobic (repellent) or hydrophilic, acid resistance, light reflection. The metal oxide may further comprise functional doped materials for use as markers or for altering the coated layer resulting in tailored made functional surface. Thus the coated film according to the present invention may comprise colors, electroactive components, metal-nanoparticles, dopants suitable for sensing, biochemicals or luminescent molecules.

Furthermore, the present invention facilitates the formation of functionalized graded materials. In such materials where thin nanostructured layers of coating are applied on a substrate, rather than obtaining homogeneity (one homogenous layer) it is desired to obtain non-homogenous layers. Such materials with spatially non-homogenous layers impart properties utilized in many applications. Ceramic coatings and film technology are two fields greatly benefiting from such non-homogenous coatings. The improvement in the physical/chemical and/or physical/mechanical properties of such materials are for example, wear resistance, durability, hardness, corrosion resistance. Their preparation however, is rather complicated requiring monolayer or multilayer coating of films frequently based on nanostructured high melting compounds.

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Such graded materials may easily be obtained according to the present invention by conducting the electrochemical sol-gel process with a solution having desired dopants. Conducting the electrochemical process at varying voltage results in the deposition of non homogenous layers where at each different voltage there is
5 deposited a layer having a different ration between the dopant and the sol-gel. In case metal ions are the dopants, the resulting coated film will have non homogenous layers varying in the ratio of metal to metal oxide in each layer. In case the dopant is a colored entity or optically active molecules the resulting process carried by varying the potential during the reaction will result in non-
10 homogenous layers with regards to color or optical properties. The dopants within the sol-gel precursor may further be organic, inorganic or bioorganic catalysts, chemical and biochemical sensors.

The selective sol-gel coating on conducting surfaces aided by electrodeposition of the present invention is a selective method for coating
15 complex submicrometric-size particles. Such submicron-size patterns may be printed chips or inner microscopic tubes where selective and specific coating is desired. The possibility of selectively engineering the microstructure enables the formation of capacitors and specifically minicapacitors, integrated and printed circuit boards, and flat panel displays.

20 As opposed to simple dip coating which is unspecific by the fact that all the surface of the dipped material is coated non-selectively, the coating according to the present invention is specific, where only conducting surfaces are coated. Furthermore, the thickness of a surface obtained by dip coating is random and usually is several tens of nanometer, whereas according to the present invention,
25 the thickness of the coating film is controllable and may be up to several hundreds of nanometer. The difference is demonstrated in **Fig. 2** and **Fig. 3** which show high resolution scanning electron microscopy (HR-SEM) images and electron diffraction spectroscopy (EDS), respectively, of a gold mesh coated with TiO_2 . Comparative coating was done by dip coating and by the method of
30 the present invention. Comparing 2(b) to 2(c) of the HR-SEM as well as 3(b) and

3(c) to 3(d) and 3(e) of the EDS demonstrates the difference in thickness of coating achieved by the two techniques.

As the coated material's dimension become smaller, selectivity and specificity become crucial and more difficult to achieve. **Figs 4 and 5** demonstrate such selectivity where an aluminum pattern sputtered on a silicon wafer is selectively coated with ZrO_2 and TiO_2 , respectively. **Fig. 4(a)** shows the HR-SEM of aluminum coated wafer. The aluminum complex pattern is demonstrated. Dip coating the silicone wafer in a ZrO_2 solution results in a non specific coating of the entire wafer as shown in the EDS image at **Fig 4(d)**.
10 Contrary to the non specific coating achieved by dip coating, employing the electrodeposition of the present invention yields selective coating only of the aluminum surface as shown in the EDS image at **Fig 4(g)**. A similar result was obtained in the case where the same silicon wafer having aluminum sputtered thereon was coated with TiO_2 either by dip coating as shown in **Fig. 5(d)**
15 compared to its coating by the electrodeposition method of the present invention as shown in **Fig. 5(h)**.

The specificity of the electrodeposition method of the present invention and its ability to selectively coat submicrometric size patterns may be attributed to the submicrometric size particles which are the coating particles. This is
20 demonstrated in **Fig. 6**, where a rough surface coated by the electrodeposition sol-gel process of the present invention becomes smoother. An indium tin oxide (ITO) plate has a roughness value of 7.622 (RMS value) and an average height of kinks of about 34nm (**Fig. 6(a)**). Dip coating results in smoothing of the surface reducing the roughness value to 0.615 nm and the average kinks height is
25 reduced (visually seen in **Fig. 6(b)**). Using the electrodeposition method of the present invention further reduces the roughness values to either 0.568 or 0.522 nm depending on the applied voltage (-0.9 V and -1.4 V, respectively). Furthermore, the average height of the kinks is further reduced (visually seen in **Figs. 6(c) and 6(d)**). The result of smoothing of a rough surface by the
30 electrodeposition according to the present invention further to what is achieved in

a dip coating method may be attributed to the fact that the submicrometric size particles or clusters involved in the process are driven more specifically to fill the rough contours.

It should be born in mind that the voltage range which may be employed varies depending on the nature of the coated metal. Taking an ITO plate, the upper value is about +2.5 V versus Ag/AgBr, because considerable oxygen evolution occurs above this voltage. The negative voltage in such a plate is limited to up to -1.6 V where at higher negative voltage values there occurs considerable hydrogen evolution. Water must be present in order to achieve effective coating and its presence is required both in acidic or basic conditions (**Fig. 7**). Apparently, the results in **Fig. 7** demonstrate that the effect of added water on the thickness of the resulting film passes through a maximum by applying either a negative or a positive potential, where these two different conditions display a similar behavior. Almost no film buildup is observed when no water is present.

Film thickness obtained by simple dip coating is about 55 nm. Film thickness using the electrodeposition coating of the present invention may be from several tens of nm to several hundreds on nm by variation of the applied potential. Film coating rapidly builds up during the first 15 minutes after the voltage is applied after which an almost constant thickness is reached (**Fig. 8**). This time-dependence behavior of the film coating is explained by measuring the decrease in current as a function of the applied potential (negative or positive) shown in **Fig. 9**. **Fig. 9** demonstrates that regardless of the initial applied potential, after about 15 minutes the current density reaches an almost constant value. This is explained by the fact that building of the film, i.e. coating the electrode with insulating oxides blocks the electrode surface towards electroactive species. The electrode surface is masked by the formed film and the ability to carry on the reduction or oxidation process by the electrode is greatly diminished. The correlation of times observed in figures 8 and 9 suggests that the film grows rapidly for the first 10-15 minutes after which a steady state current (regardless

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of the applied potential) is achieved which does not contribute considerably to further build up of a film.

Film thickness depends on the nature of the substrate coated. In Au compared to ITO, reduction kinetics are more facile (Fig. 9(e)) therefore Au is coated with a thicker film. This is demonstrated in Table I.

Table I: Dependence of film thickness on deposition method and nature of electrode

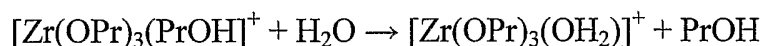
Method	Thickness	
	on ITO	on Au
Dip coating	50±10	60± 10
-0.9 V, 30 minutes	70±10	100±10
-1.4 V, 30 minutes	280±10	560±10

Comparison of the curves 6(a) - 6(d) with the curve 6(e) shows that the decrease in current density is much steeper for Au than for ITO, suggesting that the film forming on Au is faster than on ITO. The steady state residual current in Au reduction is higher than that for ITO reduction; however, it does not lead to substantial film thickening.

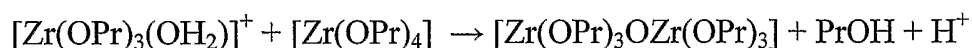
As mentioned, the electrochemical sol-gel process according to the present invention enables to carry the deposition of the transition metals either using positive potentials or negative potentials, where the former process is an acid catalyzed polymerization process and the latter process is a base catalyzed polymerization process. Turning to **Fig. 10**, the possibility of the coating reaction to be a basic or acidic catalyzed reaction is demonstrated with regards to a precursor Zr(OR)_4 forming a coating of ZrO_2 . The conductive surface is immersed in a solution comprising the sol-gel precursor Zr(OR)_4 , the alcohol ROH and trace (several hundreds of ppm) of water. The electrode which is the conducting surface is subjected to either a negative or to a positive potential. Upon the application of a positive potential of up to (+2.5 V) relative to an

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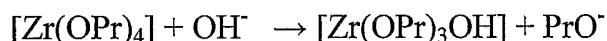
AgBr/Ag electrode, solvated H^+ species are formed which catalyze the acidic chemical transformation of $Zr(OR)_4$ to ZrO_2 on the electrode e.g. conducting surface. Upon application of a negative potential of up to (-1.8 V) relative to AgBr/Ag electrode, solvated OH^- species are formed which catalyze the basic chemical transformation of $Zr(OPr)_4$ to ZrO_2 on the electrode e.g. conducting surface. The electrochemical process generates both H^+ and OH^- even in the absence of water. As already explained and shown in **Fig. 7**, water is crucial for the coating process implying that water is involved not only in the electrochemical process but also in the coating process. Under oxidative conditions (positive potential), H^+ species are formed which protonate $[Zr(OPr)_4]$ to $[Zr(OPr)_3(PrOH)]^+$ (Pr = propanol). Nucleophilic substitution takes place in the presence of water to form $[Zr(OPr)_3(H_2O)]^+$:



The produced monoprotonated species condenses to form Zr-O-Zr bonds by reacting with another monomer molecule (either hydrolyzed or not), releasing either a water molecule, propyl alcohol or dipropyl ether:



Under reductive conditions (negative potential), OH^- species are formed forming initially $[Zr(OPr)_3(OH)]$ which by nucleophilic substitution releases a PrO^- species:



The monohydroxylated species condenses with another monomer to form the desired Zr-O-Zr bonds on the electrode (conductive surface) by a hydrolytic mechanism:



The role of the trace amount of water is to primarily provide the nucleophile which upon formation attacks the $[Zr(OPr)_4]$ sol-gel precursor to form $[Zr(OPr)_3(OH)]$. Such a mechanism is supported by the fact that most of the cathodic current is attributed to the reduction of the solvent.

30 Examples

Example 1: Coating a gold mesh with TiO_2 thin film.

Titania (TiO_2) deposition solution was prepared by adding 16.15 mL of dry 2-PrOH that was wetted with 160 ppm water and 0.1 M LiClO_4 to 0.95 mL
5 $\text{Ti}(\text{OPr})_4$ under vigorous stirring (monomer concentration was ca. 0.2 M). During the electrochemical deposition, a potential of -1.4 V vs. Ag/AgBr was applied for duration of 15 min while stirring the solution. High resolution scanning electron microscope (HR-SEM) Sirion (FEI Company) was used to produce either electron micrographs or element analysis measurements (EDS, Energy
10 Dispersive X-ray Spectroscopy).

Example 2: Coating aluminum sputtered on a silicone with TiO_2 film

The same titania solution of Example 1 was used and a potential of -1.4 V vs. Ag/AgBr was applied for duration of 15 min while stirring the solution.
15

Example 3: Coating aluminum sputtered on a silicone with ZrO_2 film

The Zr-deposition solution was prepared by adding 5 mL of dry 2-PrOH that was wetted with 900 ppm water and 0.1 M LiClO_4 to 5 mL $\text{Zr}(\text{OPr})_4$ under vigorous stirring (monomer concentration was ca. 1.12 M). Dip coating was
20 performed by pulling the substrate at a rate of $50 \mu\text{m}\cdot\text{sec}^{-1}$ from the deposition solution while stirring. During the electrochemical deposition, a potential of -1.4 V vs. Ag/AgBr was applied for duration of 30 min, while stirring the solution. High resolution scanning electron microscope (HR-SEM) Sirion (FEI Company) was used to produce either electron micrographs or element analysis
25 measurements (EDS, Energy Dispersive X-ray Spectroscopy).

CLAIMS:

1. An electrochemical method for depositing a thin film comprising metal oxides or silicon oxides on a conductive surface comprising:

(i) providing conductive surface;

5 (ii) immersing said surface in a solution comprising sol-gel precursor monomers comprising metal, transition metal or Si compounds, alcohol, a determined amount of water and an inert soluble salt;

(iii) carrying out electrodeposition process by applying low voltages to create negative or positive potential for a predetermined period of time to induce sol-gel

10 reaction at the conductive surface, thereby obtaining conductive surface coated with a thin film having desired thickness and comprising oxides of silicon and/or metal and/or transition metal formed in said sol-gel reaction.

2. A method according to claim 1 for depositing the thin film on the conductive surface carried by a non-conductive substrate, the method

15 comprising:

(i) providing a non-conductive substrate carrying a pattern formed by at least one conductive surface region on said substrate;

(ii) immersing said substrate in a solution comprising sol-gel precursor monomers or pre-polymers comprising metal, transition metal or Si compounds,

20 an alcohol, a determined amount of water and an inert soluble salt;

(iii) carrying out electrodeposition process by applying substantially low voltages to create negative or positive potential for a determined period of time to induce selective sol-gel reaction occurring at the conductive surface to produce sol-gel thin film of a desired thickness comprising oxides of silicon, metal or transition

25 metal,

thereby obtaining the pattern on the non-conductive substrate formed by the at least one conductive surface region coated with the sol-gel thin film surrounded by non-conductive regions of the substrate.

3. A method according to claim 2 wherein the low voltages create a positive potential for a determined period of time to induce selective sol-gel reaction occurring at the conductive surface to produce sol-gel thin film of a desired thickness comprising oxides of silicon, metal or transition metal.
- 5 4. A method according to claim 2 wherein said sol-gel precursor is selected from metal, transition metal or silicon alkoxide monomers or ester monomers or monomers of the formula $M(R)_n(P)_m$, wherein M is a metallic or semi metallic element or Si, R is a hydrolyzable substituent, n is an integer from 1 to 4, P is a non polymerizable substituent and m is an integer from 0 to 3, or partially
10 hydrolyzed and partially condensed polymer thereof, or any mixture thereof.
5. A method according to claim 4 wherein the sol-gel precursors are silicon alkoxide monomers, or silicon ester monomers, or monomers of the formula $Si(R)_n(P)_m$, where R is a hydrolyzable substituent, n is an integer from 1 to 4, P is a non polymerizable substituent and m is an integer from 0 to 3, or partially
15 hydrolyzed and partially condensed polymer thereof, or any mixture thereof.
6. A method according to claim 4 wherein the sol-gel precursors are titanium alkoxide monomers, or titanium ester monomers, or monomers of the formula $Ti(R)_n(P)_m$, where R is a hydrolyzable substituent, n is an integer from 1 to 4, P is a non polymerizable substituent and m is an integer from 0 to 3, or
20 partially hydrolyzed and partially condensed polymer thereof, or any mixture thereof.
7. A method according to claim 1 wherein the sol-gel precursors are zirconium alkoxide monomers, or zirconium ester monomers, or monomers of the formula $Zr(R)_n(P)_m$, where R is a hydrolyzable substituent, n is an integer
25 from 1 to 4, P is a non polymerizable substituent and m is an integer from 0 to 3, or partially hydrolyzed and partially condensed polymer thereof, or any mixture thereof.
8. A method according to claim 5 wherein several sol-gel precursor are used together in a mixture, to afford a sol-gel material which is a composite
30 containing different metal and/or semi metal elements in the final product.

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9. A method according to anyone of the preceding claims wherein the determined amount of water is such that the water/precursor monomers molar ratio is in the range 10^{-5} to 10^{-1} .
10. A method according to claim 4 wherein the sol-gel precursor is in the form of $R'_m-X-(OR)_n$, and the alcohol is ROH, wherein X is a metal, transition metal or silicon, R' is an alkyl, or aryl optionally substituted with amine, or thiol, $n+m = 4$, and R is a C_{1-3} -alkyl, preferably methyl or ethyl.
11. A method according to anyone of the preceding claims wherein the film thickness is from about 10 nm to about 1000 nm.
- 10 12. A method according to claim 1-3 wherein the oxide formed in step (iii) is silicon oxide, or metal oxide or transition metal oxide or mixture of such oxides.
13. A method according to claim 12 wherein the transition metal or metal oxide coating comprises oxides of zirconium, aluminum, titanium, iron, tungsten, nickel, vanadium or cobalt and their mixtures.
- 15 14. A method according to claim 1-3 wherein the deposited thin film further comprises doped materials selected from the group consisting of colors, metal particles, dopants suitable for sensing, biochemicals or luminescent molecules.
15. A method according to claim 1-3 wherein said substantially low voltage does not exceed a few voltages in its absolute value.
- 20 16. A method according to claim 15 wherein said voltage is between (-1.7) V to $(+2.6)$ V vs. Ag/AgBr and for duration of from about 5 minutes to about 45 minutes.
17. A method according to claim 1-3 wherein said negative or positive potential induces electrochemical formation of solvated H^+ or OH^- that catalyzes
- 25 said sol-gel reaction at the conductive surface.
18. A method for depositing a thin film on the conductive surface carried by a non-conductive substrate, the method comprising:
- (i) providing a glass substrate carrying a pattern formed by at least one conductive surface region of indium tin-oxide placed thereon;

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(ii) immersing said glass/indium tin-oxide in a solution comprising $\text{Zr}(\text{O-isopropyl})_4$, isopropanol, 900 ppm water and LiClO_4 ;

(iii) carrying out electrodeposition process by applying substantially low voltage of 1V-2.2 V for a determined period of 15 to 30 minutes so as to induce selective

5 sol-gel reaction occurring at the conductive surface to produce ZrO_2 thin film.

19. ZrO_2 thin film obtained by the method of claims 1 -3.

20. A method of smoothening a conductive surface having submicrometer roughness by subjecting said surface to an electrochemical sol-gel process according to claim 1.

10 21. A method according to claim 20 providing for reducing the roughness of said surface to a few nanometers or less roughness.

22. A method according to claim 20 wherein the conductive surface is the surface of an ITO electrode.

23. Conductive surface obtained by the method of claim 20 or 21.

15 24. A patterning method, comprising providing a non-conductive substrate carrying a pattern of spaced-apart conductive portions and subjecting said substrate to the method of Claims 1 to 16, by using the sol-gel precursor monomers solution that further comprises metal ions.

25 25. A device comprising a patterned structure produced using the method according to any one of Claims 2 to 17.

26. A device comprising a patterned structure produced using the method according to claim 24.

27. A capacitor formed by incorporating a dielectric spacer produced by the method of any one of claims 1 to 20 between the capacitor plates.

25 28. An integrated device comprising a stack of layers having different optical properties, said layers being deposited according to any one of claims 1 to 6.

29. An integrated device comprising a stack of layers having different electrical conductivities, said layers being deposited according to any one of
30 Claims 1 to 6.

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30. A display device comprising an array of cathode elements arranged in a spaced apart relationship on a non-conducting substrate, said cathode elements being coated with a photosensitive material using the selective coating according to any one of claims 1 to 8.

5 31. A functionalized graded material comprising at least two thin films obtained by sequential deposition on a conductive surface using the deposition method of claims 1-16 and using timely varying value of the negative or positive potential.

10 32. A functionalized graded material according to claim 31 wherein the doped material as defined in claim 15 in the deposited thin film is metal particles, thereby said at least two layers thereby having different ratio of metal to metal oxide.

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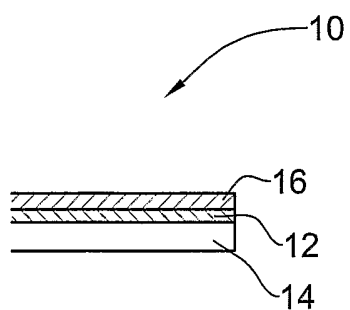


FIG. 1A

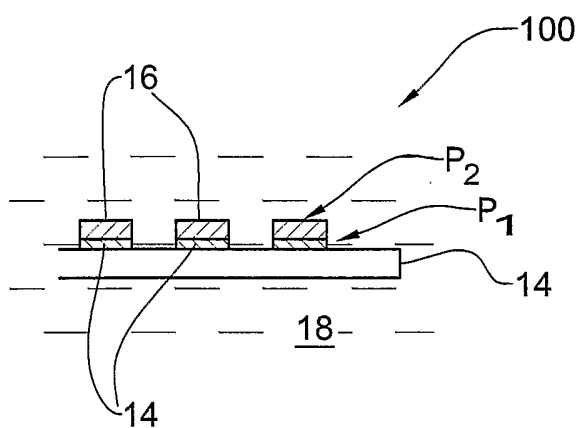


FIG. 1B

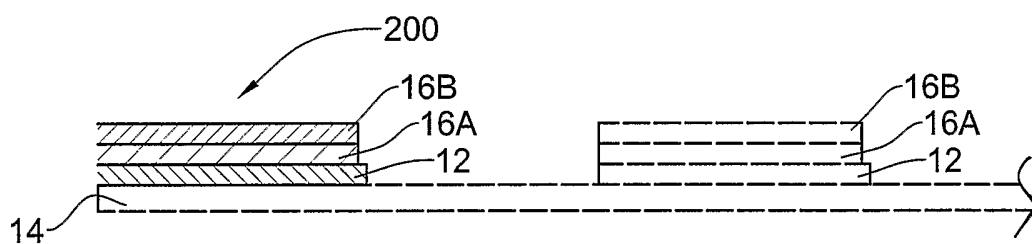


FIG. 1C

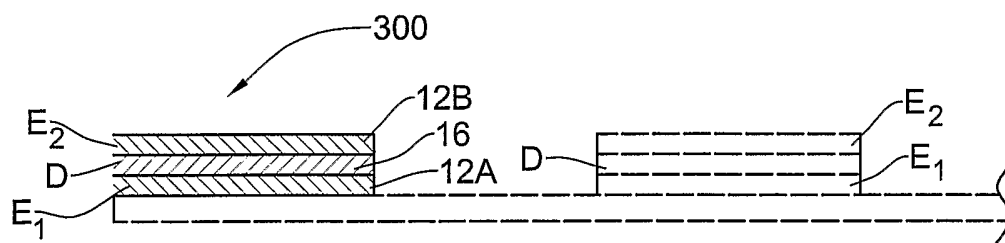


FIG. 1D

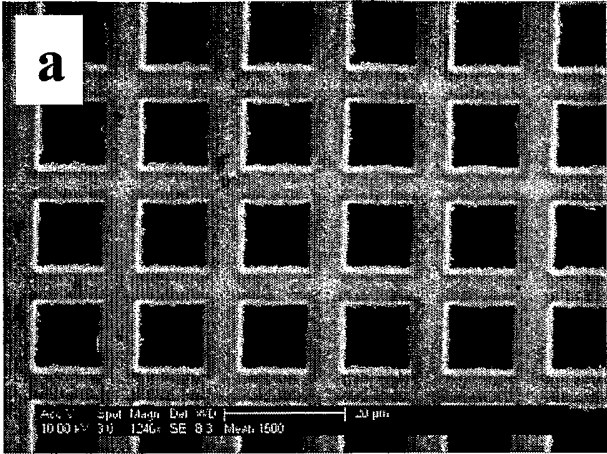


FIG. 2A

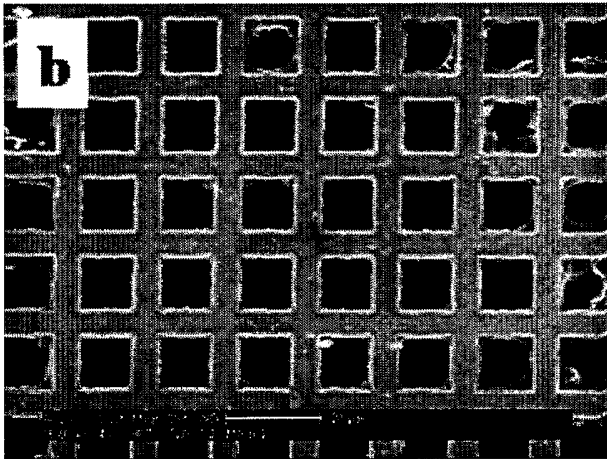


FIG. 2B

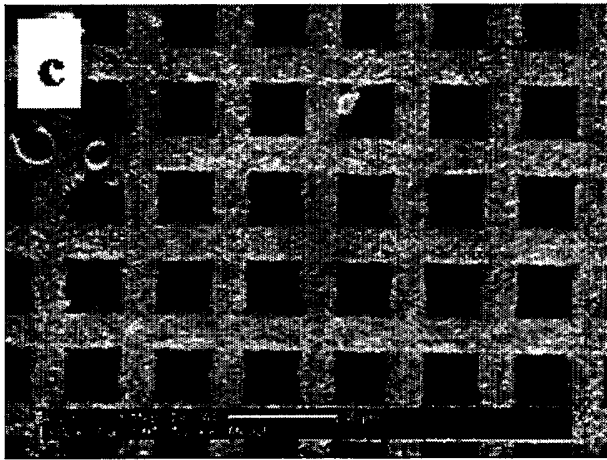


FIG. 2C

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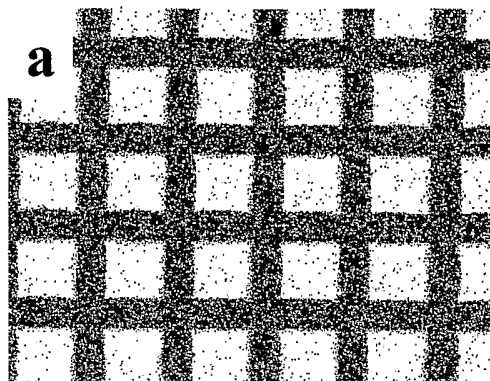


FIG. 3A

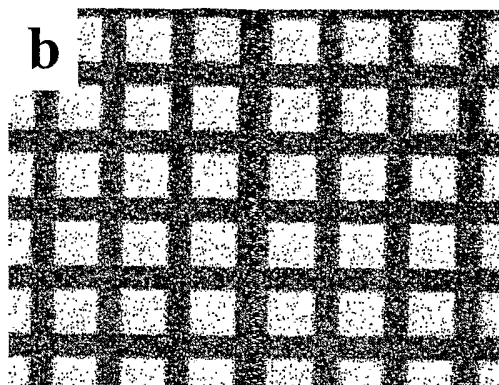


FIG. 3B

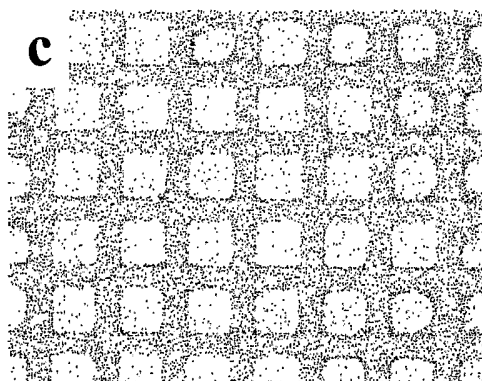


FIG. 3C

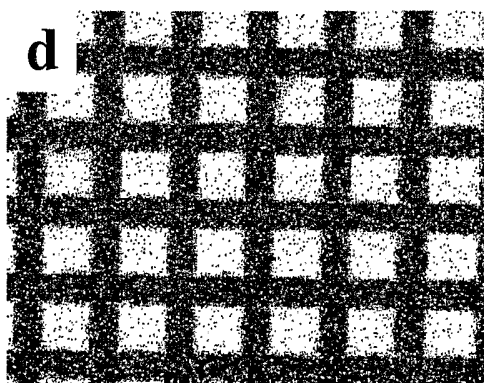


FIG. 3D

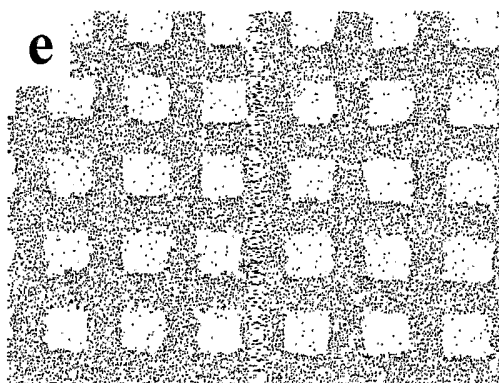
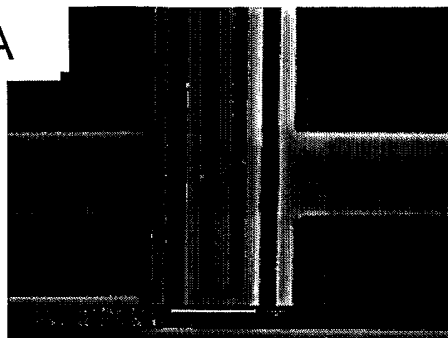


FIG. 3E

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FIG. 4A



b

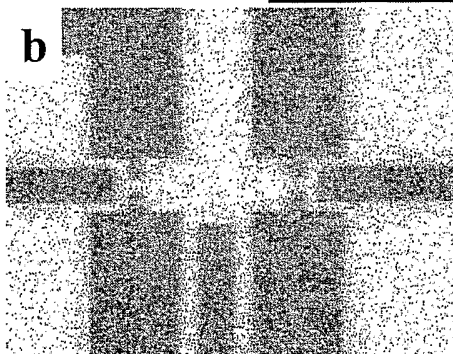


FIG. 4B

c

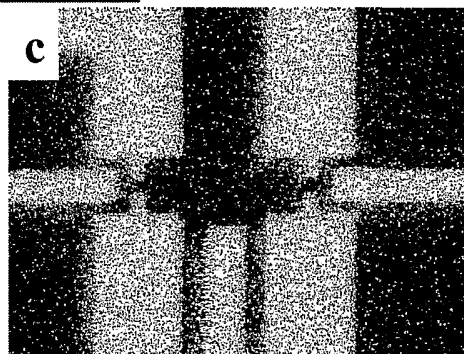


FIG. 4C

d

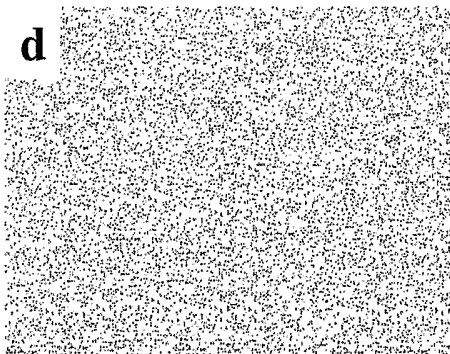


FIG. 4D

e

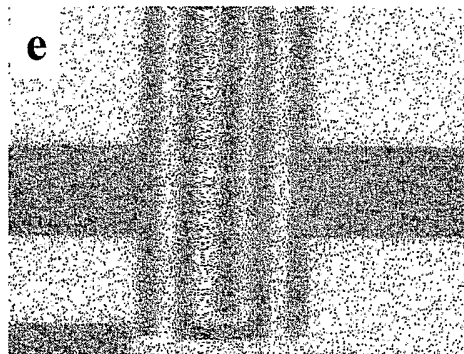


FIG. 4E

f

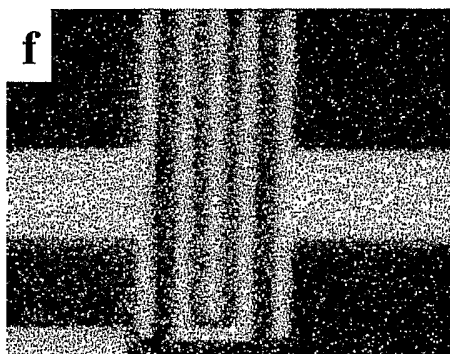


FIG. 4F

g

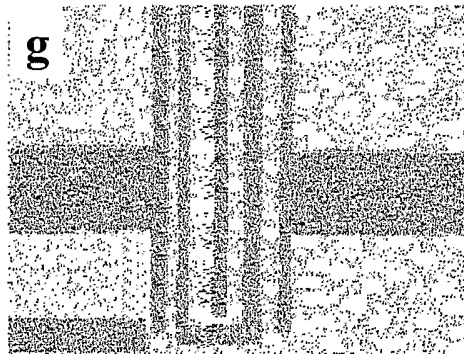


FIG. 4G

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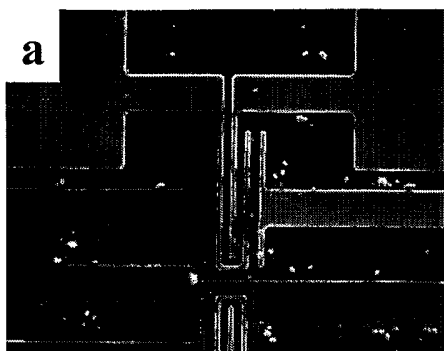


FIG. 5A

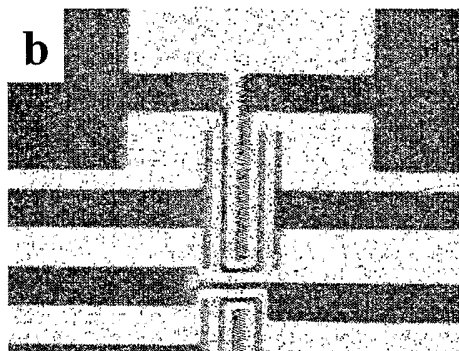


FIG. 5B

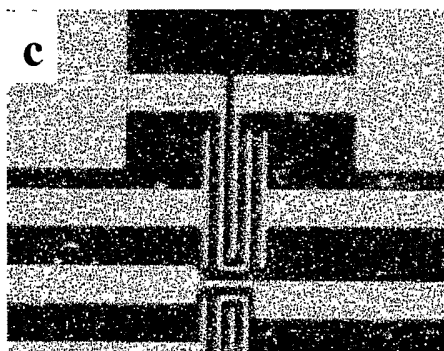


FIG. 5C



FIG. 5D

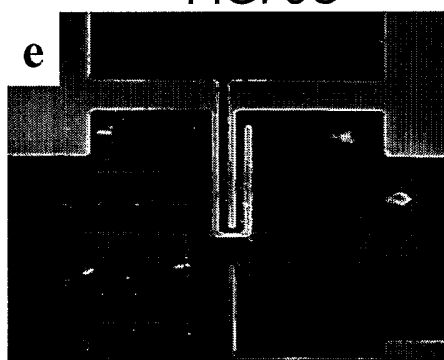


FIG. 5E

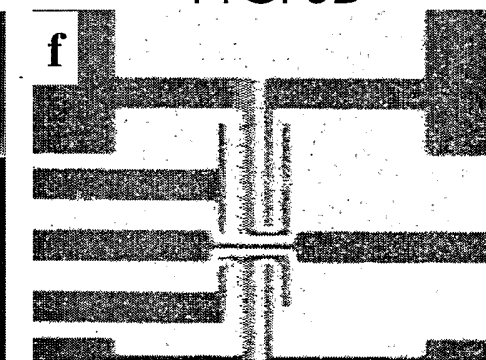


FIG. 5F

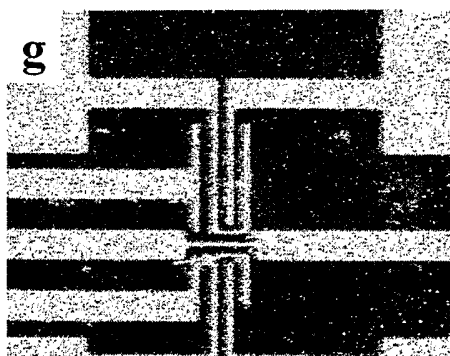


FIG. 5G

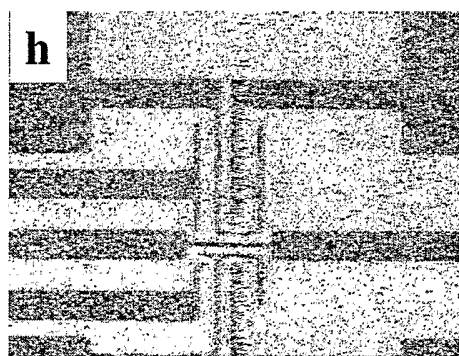


FIG. 5H

FIG. 6A

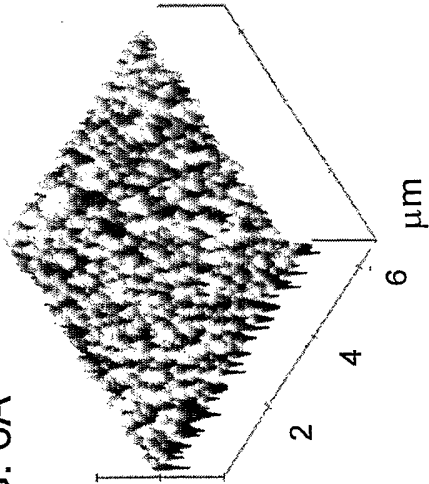


FIG. 6B

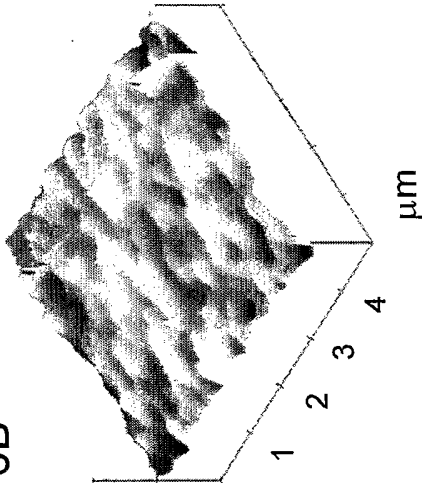


FIG. 6C

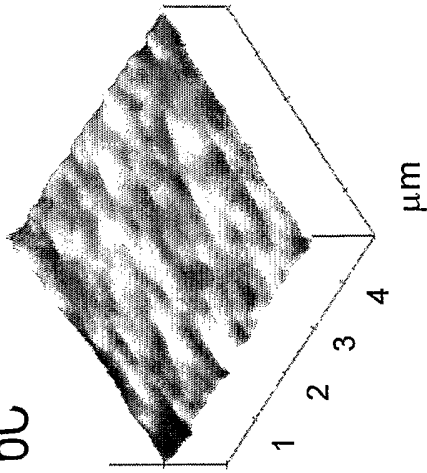
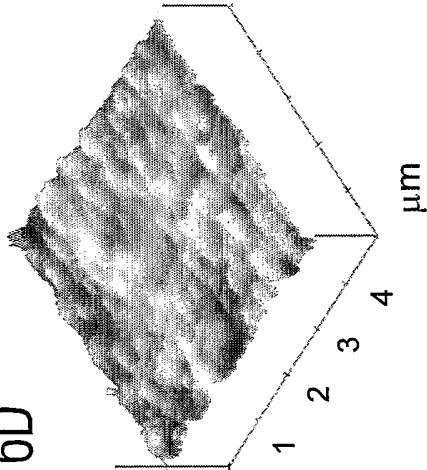


FIG. 6D



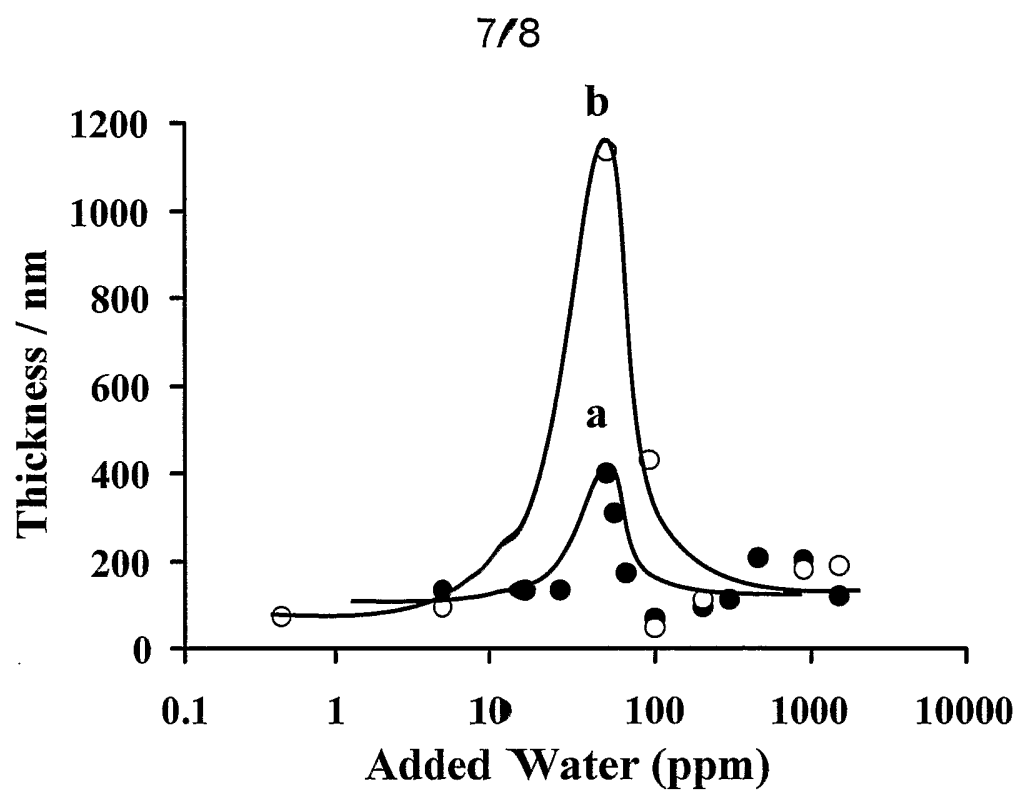


FIG. 7

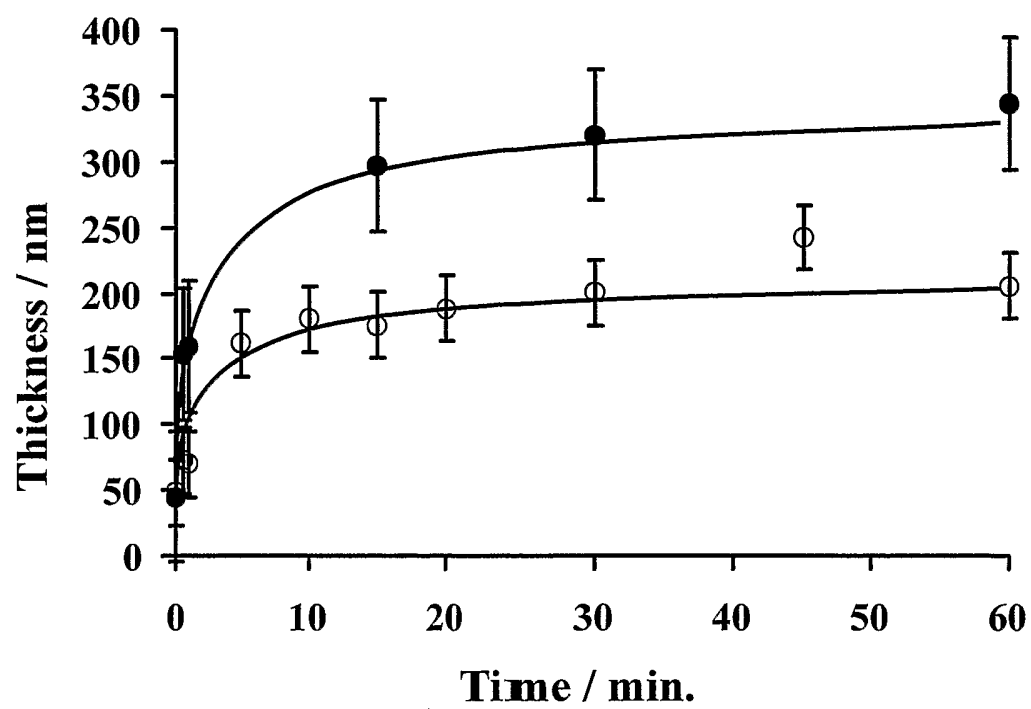


FIG. 8

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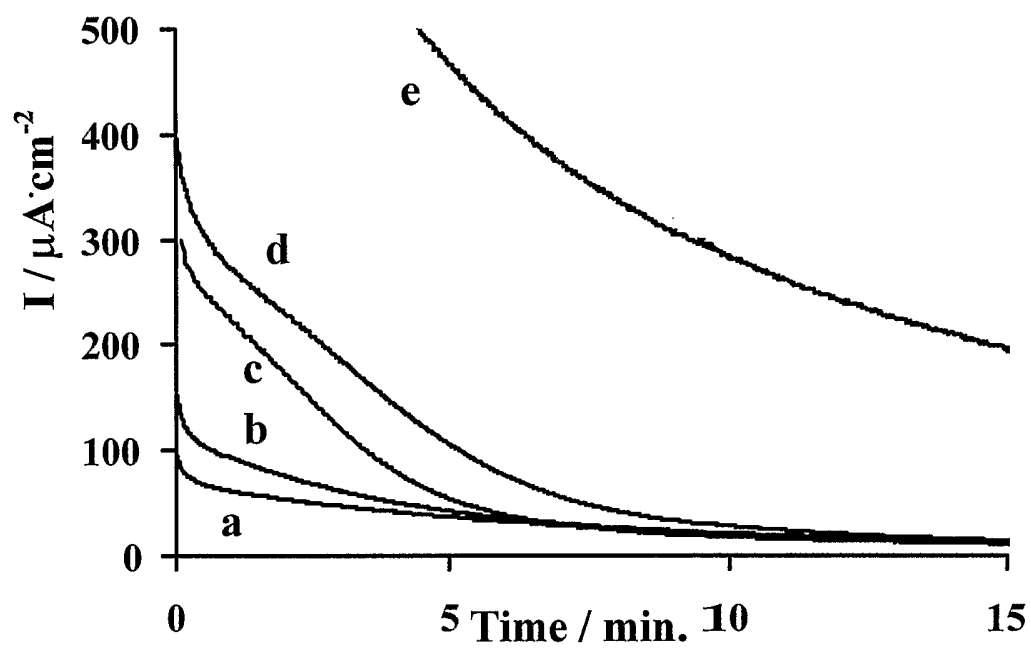


FIG. 9

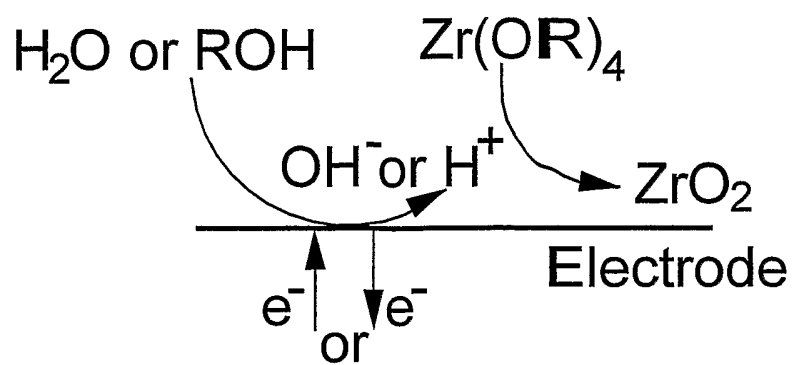


FIG. 10

INTERNATIONAL SEARCH REPORT

Int. Application No.
PCT/IL2005/000393

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C25D9/04

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)

IPC 7 C25D

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	SHACHAM R ET AL: "ELECTRODEPOSITION OF METHYLATED SOL-GEL FILMS ON CONDUCTING SURFACES" ADVANCED MATERIALS, VCH VERLAGSGESELLSCHAFT, WEINHEIM, DE, vol. 11, no. 5, 22 March 1999 (1999-03-22), pages 384-388, XP000827258 ISSN: 0935-9648 cited in the application	1-5, 11, 12, 15-17, 20-32
A	page 385, column 1, line 8 - page 386, column 1, line 34 page 387, column 1, paragraph 2 page 387, column 2, paragraph 4 ----- -/--	9

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in 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 document 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.

Z document member of the same patent family

Date of the actual completion of the international search

9 September 2005

Date of mailing of the international search report

19/09/2005

Name and mailing address of the ISA

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Authorized officer

Zech, N

INTERNATIONAL SEARCH REPORT

International Application No
PCT/IL2005/000393

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 747 727 A (SAWADA ET AL) 5 May 1998 (1998-05-05)	1,2,4,5, 7,8, 10-13, 19-21, 23-26
A	examples 1-3 claims 1-4,13-18,21-23,25 -----	3,9,15, 18
X	HIDEKI NISHIMORI ET AL: "PREPARATION OF THICK SILICA FILMS IN THE PRESENCE OF POLY(ACRYLIC ACID) BY USING ELECTROPHORETIC SOL-GEL DEPOSITION" JOURNAL OF SOL-GEL SCIENCE AND TECHNOLOGY, KLWER ACADEMIC PUBLISHERS, DORDRECHT, NL, vol. 7, no. 3, October 1996 (1996-10), pages 211-216, XP000630229 ISSN: 0928-0707 cited in the application	1,2,4,5, 10,12, 20,21, 23-26
A	page 211, column 2, line 18 - page 212, column 1, last line page 212, column 2, lines 25,26 -----	9
A	US 5 925 228 A (PANITZ ET AL) 20 July 1999 (1999-07-20) paragraphs '0031!, '0032!, '0035! -----	1-5, 8-10,12

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No
PCT/IL2005/000393

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US 5925228	A	20-07-1999	NONE	