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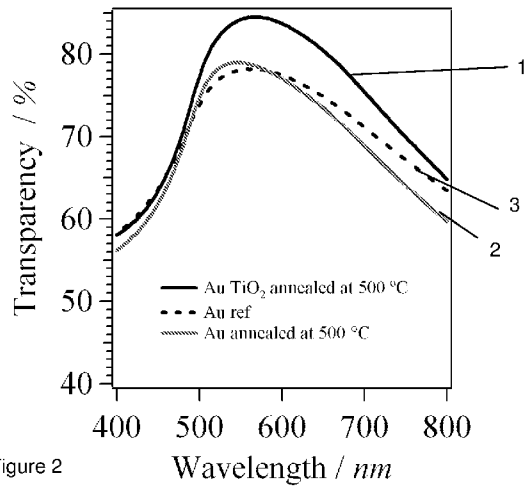

Figure 2

(57) Abstract: A method of producing a thin film structure such as a transparent electrode. A transparent thin film of a first metal such as gold or silver is deposited on a substrate. There is then deposited on the thin film of the first metal a compound of a second metal which forms a continuous, transparent thin film of an oxide of the second metal on the film of the first metal. The substrate carrying the thin films is annealed at a temperature of at least about 300 °C. The compound of a second metal that is deposited on the first metal may be a precursor that is treated, for example by heat, so as to produce the oxide of the second metal. The precursor may be an organometallic compound of the second metal; or a hydroxide of the second metal; or a sol of nanoparticles of the oxide of the second metal mixed with an organometallic precursor of the oxide of the second metal. The precursor may be deposited as a liquid. The oxide may be TiO_x, WO_x, MoO_x, VO_x, TaO_x, ZnO_x, NiO_x or AIOx..

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Stabilising Thin Metal Films On Substrates

This invention relates to stabilising thin metal films on substrates. The invention is particularly, but not exclusively, concerned with transparent electrodes, for example for use in semiconductor thin film devices which are used in the construction of photo-sensitive devices such as photovoltaic cells and in light emitting diodes. However, the invention is applicable to other contexts where the transparency of the structure is not essential and / or the structure is not used as an electrode.

In some embodiments the invention provides transparent electrodes for semiconductor thin film devices incorporating an organic semiconductor, for example organic photovoltaic devices and light emitting diodes. However the electrodes are capable of use in a wide range of applications, including devices based on inorganic semiconductors.

Very thin, for example less than or equal to about 20 nm or more preferably about 15 nm, metal films are an attractive alternative to conducting oxides as the transparent electrode for a wide variety of applications including light-emitting diodes and photovoltaics. Advantages of thin metal film electrodes include their simplicity, ease of processing using roll-to-roll thermal evaporation, compatibility with flexible substrates and chemical homogeneity as compared to the complex ternary oxides, such as indium tin oxide or zinc tin oxide which are the currently the most widely utilised transparent electrode materials.

For many applications silver (Ag), gold (Au) and platinum (Pt) are the metals of choice due to their relatively high intrinsic resistance to oxidation, which removes / or greatly reduces the requirement to preclude air during the various device fabrication stages. Optically thin metal films of many metals do not have a self-limiting oxide and so may completely oxidise. In recent years optically thin Ag films have received attention as the transparent electrode in organic photovoltaic devices and optically thin Au films have shown promise as the transparent electrode in efficient organic light-emitting diodes. Au is already used extensively in the electronics industry to provide reliable interconnects, and thermal control coatings for windows. It is also the electrode material of choice for emerging field of nano-electronics and nano-photonics. With the advent of ultra-thin (< 100 µm) glass,

flexible metal electrodes can be achieved with the advantage of the barrier properties and thermal stability of glass.

It is not possible to fabricate robust sub-10 nm films of many technologically important metals, including gold, silver and copper (Cu), on glass without the use of an interfacial adhesion layer. One established class of adhesive layer for the preparation of Au, Ag and Cu films on glass is the deposition of a 1-10 nm film of a transition metal (e.g. Ge, Ni, Cr and Ta.) However the use of metal adhesion layers is sub-optimal for the preparation of highly transparent metal films since the adhesion layer itself makes a significant contribution to total film absorption. As an alternative, monolayers of molecules capable of binding to both the substrate and incoming metal have proved to be particularly effective. For example (3-mercaptopropyl)trimethoxysilane (MPTMS) can be used as a molecular adhesive for the preparation of robust optically thin Au films on glass without contributing to light absorption. It has been shown that sub-10 nm Au films supported on a mixed monolayer of MPTMS and (3-aminopropyl)trimethoxysilane (APTMS) on glass are remarkably robust towards ultra-sonication in various solvents and mechanical abrasion with a very low root mean square (rms) roughness (~0.4 nm over a 5 µm x 5 µm area) making them suitable for a variety of applications, where chemically stable, electrically conductive and transparent electrodes are required.

WO2012/001424 discloses that in general the use of a first silane which is a non-amino functional silane and a second silane which is an aminofunctional silane is advantageous.

Optically-thin films of metals on glass modified with a molecular monolayer would not be expected to be resistant to high temperatures (> 300°C) owing to the suppressed melting point and thermodynamic instability stemming from the high surface to volume ratio, both of which scale with film thickness and the relatively low desorption temperature of chemisorbed silanes. It has been shown that sub 15 nm Au films on MPTMS detivatized glass are not stable to even mild heating, for example Doron-Mor *et al.* [Chemistry of Materials *16* (2004) 3476-3483]. WO2012/001424 discloses that at temperatures above 300°C apertures form in sub-10 nm Au films supported on glass derivatized with MPTMS and APTMS. From a technological perspective this severely limits the application of optically thin metal

films prepared using molecular adhesives on glass to those involving relatively low temperature processing steps, i.e. carried out at temperatures of less than about 300°C.

WO2012/001424 discloses a method for the preparation of robust ultra-thin metal film electrodes on glass and plastic substrates. The method involves the use of a mixed molecular monolayer deposited from the vapour phase as an adhesion promoter for ultra-thin (< 10 nm) metal films particularly Au, Ag and Cu.

The current invention relates to a method of making thin metal films (such as less than or equal to about 20 nm or about 15 nm) supported on substrates of e.g. glass, which are robust towards temperatures significantly higher than 300°C, so that that they can be used for example as transparent electrodes in applications requiring a high temperature processing step. The metal films may be continuous or have apertures or other features prior to high temperature processing.

Viewed from one aspect of the present invention, there is provided a method of producing a thin film structure, wherein a transparent thin film of a first metal is deposited on a substrate; there is deposited on the thin film of the first metal a compound of a second metal which forms a continuous, transparent thin film of an oxide of the second metal on the film of the first metal; and the substrate carrying the thin films is annealed at a temperature of at least about 300°C.

The compound containing the second metal may be the oxide of the second metal, which typically may be deposited by sputtering or evaporation. Another way of depositing the oxide would be to deposit a sol of nanoparticles of the oxide of the second metal mixed with a binder, which could be treated, for example by heating, to leave a layer formed from the nanoparticles of the oxide.

However, preferably there is deposited a precursor of the oxide of the second metal that subsequently forms the continuous, optically thin layer of an oxide of the second metal after deposition. For example, the precursor of the second metal oxide may form the oxide of the second metal readily when heated, or as a result of exposure to light, or as a result of a chemical reaction.

The oxide of the second metal could be, for example, TiO_x, WO_x, MoO_x, VO_x, TaO_x, ZnO_x, NiO_x or AlO_x. Particularly when using a precursor, it may be difficult to predict exactly which oxide or mixture of oxides will be produced. For that reason the oxides are referred to above as being in the form "MO_x" although typically they could be TiO_2, WO_3, MoO_3, V_2O_5, Ta_2O_5, ZnO, Al_2O_3, or NiO. Where in this specification there is a reference to a specific oxide of a metal, it is to be understood that it is an example only and that it encompasses oxides in which the metal has other oxidation states. However, where it is necessary to identify a specific oxide it can be TiO_2, WO_3, MoO_3, V_2O_5, Ta_2O_5, ZnO, Al_2O_3, or NiO as appropriate.

In the case of TiO_2 the TiO_2 film may be prepared by depositing an oxide precursor in the form of a layer of titanium (IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$) in n-butanol which converts to a dense layer of TiO_2 when heated.

In the case of MoO_3 the MoO_3 film may be prepared by depositing an oxide precursor in the form of a solution prepared by dissolving MoO_3 in hydrogen peroxide (H_2O_2) to form a hydroxide of molybdenum and mixing with polyethylene glycol to adjust the concentration and viscosity. This film converts to a dense layer of MoO_3 when heated.

In general, in this specification the term “precursor” is used to denote a substance, other than the second metal or the oxide of the second metal itself, which is deposited and is then treated to form the oxide of the second metal. The precursor could for example comprise an organometallic compound of the second metal, or a hydroxide of the second metal, or a sol of nanoparticles of the oxide of the second metal mixed with an organometallic precursor of the oxide of the second metal. Examples of precursor materials are: ZnO films can be prepared from a solution of zinc acetate dihydrate and ethanolamine in alcohol. The Zn acetate is converted to ZnO by heating in air. Tungsten Oxide (WO_x) films can be prepared from a solution of Tungsten(VI) Isopropoxide by heating in air. V_2O_5 films can be prepared from an isopropanol solution of vanadium(V) oxitriisopropoxide. Zirconium oxide (ZrO2) films can be prepared from a solution of zirconium oxychloride (ZrOCl2) mixed with 2-methoxyethanol and H_2O_2. Aluminium oxide films can be prepared from $AlCl_3$ in a solvent of acetonitrile with ethylene glycol, by heating.

When the second layer is deposited as a precursor of the oxide of the second metal rather than as the oxide of the second metal as such, the underlying layer of the first metal is more robust to elevated temperatures.

The second layer is preferably deposited as a liquid precursor, as is the case with the examples given above, but embodiments of the invention are not limited to solution processing of the precursor. The precursor, such as an organometallic compound, could be deposited by vapour deposition and then to produce the oxide of the second metal. However, when a thin oxide layer is deposited from a liquid precursor, and then treated by heat, light, chemical reaction or otherwise to form the oxide layer, its ability to protect the underlying metal from subsequent chemical reaction, such as oxidation, is better than that obtained from sputtering or evaporation. This is particularly the case when the film of the first film is patterned, since a line-of-sight deposition method such as evaporation or sputtering will not be able to cover the entire surface of the metal, such as the side edges of surface artefacts such as apertures or ridges.

In accordance with the invention, the second metal is not deposited on the first layer in metallic form and then oxidised. The oxide or, more preferably, the oxide precursor are deposited as such.

An oxide precursor may form the oxide when heated to a temperature below that at which apertures would otherwise form in the film of the first metal, such as below 300°C. In that case the substrate carrying the thin layers could be heated to that lower temperature to allow time for the oxide to form, before then being heated to 300°C or more for annealing. Thus in such a process, the optically thin layer of the first metal is capped with a continuous thin layer of an oxide of the second metal prior to reaching about 300°C. However, that is not always necessary. If the oxide precursor is applied as a liquid which is then heated so that the oxide is deposited from solution, in some cases it is possible to heat to an annealing temperature of 300°C or more, without waiting for formation of the oxide to be completed. A possible reason for this is that as the dense oxide is deposited there is compression on the underlying layer of the first metal.

By using a method in accordance with the invention, it is possible to prevent or significantly restrict the formation of apertures in the thin layer of the first metal at annealing temperatures significantly greater than about 300°C, such as up to about 400°C or about 450°C or about 500°C, or more.

In some embodiments of the invention, substantially no apertures are formed in the thin layer of the first metal as a result of heating to temperatures of greater than 300°C. In some embodiments of the invention, no more than about 5% of the surface area of the thin layer of the first layer is constituted by apertures that have been formed as a result of heating to temperatures of greater than 300°C. Such a low level of apertures would not significantly change the properties or function of the thin metal film.

Preferably, the structure is transparent, being for example in the form of a transparent electrode for use in a semiconductor thin film device.

Viewed from another aspect, the invention provides a method of producing a thin film semiconductor device comprising combining such a transparent electrode with a donor semiconductor material, an acceptor semiconductor material, and a second electrode.

Viewed from another aspect the invention provides a thin film semiconductor device comprising such a transparent electrode, a donor semiconductor material, an acceptor semiconductor material, and a second electrode.

In some embodiments the thin film semiconductor device is a photovoltaic device.

In some embodiments, at least one of the semiconductor materials is an organic semiconductor material and in some embodiments both of the semiconductor materials are organic. In accordance with some embodiments of the invention the electrode is used in an organic photovoltaic device. However, at least one of the semiconductor materials could be inorganic and in some embodiments of the invention both of the semiconductor materials are inorganic. In accordance with some embodiments of the invention the electrode is used in an inorganic photovoltaic device. It will be appreciated that in the context of an inorganic

semiconductor the expression "donor semiconductor material" encompasses a material that has been doped with an p-type impurity so as to be a p-type semiconductor material, and the expression "acceptor semiconductor material" encompasses a material that has been doped with an n-type impurity so as to be an n-type semiconductor material.

Electrodes produced in accordance with embodiments of the invention can also be useful for dye sensitised photovoltaics and photovoltaics that do not include organic semiconductors. Such photovoltaics may for example be based on inorganic semiconductor quantum dots.

In dye sensitized photovoltaics a nano-porous TiO_2, or NiO or ZnO oxide film several microns in thickness is deposited onto the transparent electrode, which traditionally has been a conducting oxide such as indium tin oxide, fluorine doped tin oxide or another conducting oxide. This will involve annealing at a temperature greater than 300°C and so the transparent substrate electrode must be robust towards elevated temperature. The surface of the nano-porous oxide is then provided with a layer of sensitizer, either dye molecules or an inorganic semiconductor. The nanostructured oxide is then back filled with a solid hole-conductor (only solid after a solvent has evaporated) or a liquid redox couple (e.g. iodide (I^-) / triiodide (I_3^-)). If a liquid electrolyte is used, and if the electrode is metal, the electrolyte can corrode the electrode. For this reason optically thin metal films are not used in dye sensitized photovoltaics, although if they could be there would be huge cost advantages, since optically thin metal film electrodes are much cheaper to produce than conducting oxides.

A thin, continuous oxide layer over the metal electrode surface, if the electrode is in accordance with the invention, would block attack by the electrolyte. It may not however be necessary to put the thin continuous oxide layer and the thick nano-porous layer down sequentially. It may be possible to deposit a single layer that phase separates to form a dense thin (for example ≤ 50 nm) continuous layer at the electrode interface.

Preferably the thin film of the oxide of the second metal has a thickness of no greater than about 50 nm, or no more than about 30 nm, or no more than about 20

nm, or no more than about 15 nm, or no more than about 10 nm. Preferably the transparent thin film of the oxide of the second metal has a thickness of no less than about 4 nm or no less than about 5 nm, or no less than about 8 nm. In some cases, the transparent thin film of the oxide of the second metal has a thickness of no less than about 0.3 nm or no less than about 0.5 nm, or no less than about 1 nm. These very low thicknesses may be appropriate if the second metal is aluminium which can form stable oxides of such thicknesses, that can have a protective effect.

In some embodiments the thin film of the first metal is no more than about 20 nm thick or no more than about 15 nm thick. In some embodiments the optically thin film of the first metal is no more that about 10 nm thick. In some embodiments, the thickness of the film of the first metal is no less than about 4 nm. In some embodiments, the thickness of the film of the first metal is no less than about 6 nm. In some embodiments, the thickness of the film of the first metal is no less than about 8 nm.

The film of the first metal can be attached to the substrate using an adhesion layer. Such an adhesion layer could be any known type of adhesion layer such as inorganic adhesion layers including transition metals and compounds such as zinc sulphide ZnS, or an organic adhesion layer such as a silane or a mixed adhesion layer, of a non-amino functional silane and an aminofunctional silane as disclosed in WO2012/001424. One suitable adhesion layer is (3-aminopropyl)trimethoxysilane (APTMS); in the case of a thin film of metal deposited on a substrate using this adhesion layer, disintegration of the metal would normally occur at 200 °C whereas in accordance with the invention there is resistance to significantly higher temperatures such as 500 °C. Thus this invention is particularly suitable for cases where the adhesion layer does not render the thin metal film robust towards elevated temperature.

The first metal could be, for example, gold, silver, platinum or copper. More generally, the first metal could be either a single metal selected from the group consisting of copper, nickel, palladium, platinum, silver, chromium, gold, cobalt or tantalum; or an alloy of two or more metals in that group; or an alloy of one or more metals in that group, together with a metal that is not in that group; or, for example

a bilayer of a metal in that group, and another metal in that group; or a bilayer of a metal in that group and a metal that is not in that group .

Where the structure is to be used as an electrode, the overlying oxide layer must have electronic functionality, i.e. conduct electrons and/or holes so as not to electrically isolate the metal film. Preferably the oxide layer has optical functionality such as, for example, to reduce reflections.

Use of the invention greatly increases the number of potential applications. For example electrodes in accordance with the invention may be used for optoelectronic applications requiring a high temperature processing step including thin film photovoltaics based on inorganic semiconductors, dye sensitized organic photovoltaics and infra-red reflective glass. The invention may be used in contexts other than electrodes. If the oxide used to coat the transparent metal film is TiO_2 the invention may be used for infra-red reflective *self-cleaning* glass, since TiO_2 is known to photo-catalytically break down carbon based material when illuminated with ultra-violet light. The invention can be applied to scenarios where it is not necessary for the substrate to be transparent, and the substrate could for example be a non transparent layer of metal oxide such as aluminium oxide or zinc oxide, or of an opaque plastics material. The invention could be applied to an element used as a heater. When an electric current is passed through the thin metal film, it will heat up. Because it is trapped under the oxide layer, it will remain robust at elevated temperatures. Where the invention is used to produce infra-red reflective glass and / or self-cleaning glass, that glass could be heated by passing an electric current through the thin metal film.

Where an oxide precursor is deposited and then heated to generate the oxide, heating may be effected by passing an electric current through the metal film.
The invention may be expressed in a number of additional forms. For example, viewed from another aspect of the invention, there is provided a transparent structure produced by a method in accordance with the first aspect of the invention.

Viewed from another aspect there is provided a method of stabilising a thin film of a first metal on a substrate, comprising the step of depositing on the thin film of the

first metal a compound of a second metal which forms a continuous, thin film of an oxide of the second metal on the film of the first metal.

Some examples in accordance with the invention will now be described by way of example and with reference to the accompanying drawings, in which:

Figures 1a, 1b and 1c show images of different samples annealed to 500°C;

Figure 2 shows plots of transparency against wavelength for three samples;

Figures 3a, 3b, 3c and 3d show AFM (Atomic Force Microscope) images of different samples heated to 500°C;

Figure 4 shows plots of transparency against wavelength for four samples;

Figures 5a and 5b show AFM images two samples heated to 500°C;

Figure 6 shows plots of current density against voltage;

Figures 7a, 7b, 7c and d show AFM images of different samples before and after heating to 500°C;

Figures 8a and 8b show AFM images of a sample before and after heating to 500°C; and

Figures 9a and 9b show AFM images of samples after heating to 500°C

In a first example, it is shown that an 8.4 nm Au film supported on glass derivatized with a mixed molecular monolayer remains continuous up to the softening temperature of the glass substrate (at approximately 500°C) without the formation of apertures, when capped with the metal oxide overlayer. With reference to Figure 1, an 8.4 nm Au film was supported on mixed monolayer (MPTMS : APTMS) derivatised glass. For the image of Figure 1 (a), the Au film was annealed to 500°C. Random apertures have formed in the film. For the image of Figure 1(b) the Au film was annealed to 500 °C (as in (a)) and then coated with an approximately 10 nm

TiO_2 film deposited from solution and annealed at 500°C. Apertures in the underlying Au film are still clearly visible. On average the size, shape and number density of said apertures in the underlying film have not significantly changed. For the image of Figure 1 (c), the Au film was coated with an approximately 10 nm TiO_2 overlayer from solution, then annealed to 500 °C. There is no evidence of aperture formation.

Figure 2 shows plots of transparency against wavelength for (1) an 8.4 nm Au film supported on mixed monolayer derivatised glass with a 10 nm TiO_2 overlayer annealed to 500 °C; (2) the same structure without the overlayer; and (3) for comparison a non-annealed 8.4 nm Au film supported on the mixed monolayer. This illustrates the improvement in far field transparency using the oxide overlayer.

In a second embodiment it is shown that 8.4 nm Au films supported on glass substrates derivatized with a mixed molecular monolayer are more robust at a temperature of about 500°C when coated with an approximately 10 nm thick oxide overlayer. To demonstrate the generality of the approach thermally evaporated WO_3 and MoO_3 and solution processed MoO_3 are also shown to be effective, although those oxides processed from solution are most effective.

Figures 3 (a), (b), (c) and (d) are AFM images of 8.4 nm Au films supported on mixed monolayer derivatised glass and heated at 500°C. 3(a) shows the results without an oxide overlayer. 3(b) shows the result with a ~10 nm evaporated WO_3 layer. 3(c) shows the result with a ~10 nm solution processed MoO_3 overlayer. 3(d) shows the result with a ~10 nm solution processed TiO_2 overlayer. Whilst the solution processed TiO_2 layer of 3(d) is the most effective the other oxide overlayers are also reasonably effective.

Figure 4 shows plots of transparency against wavelength for the 8.4 nm Au film supported on mixed monolayer derivatised glass with and without oxide overlayers annealed to 500 °C, illustrating the improvement in far field transparency. Plot 1 is for the reference material without an overlayer; plot 2 for the solution processed MoO_3 overlayer; plot 3 for the evaporated WO_3 layer; and plot 4 for the solution processed TiO_2 overlayer.

Figures 5(a) and 5(b) show AFM images of 8.4 nm Au films supported on mixed monolayer derivatised glass coated with: 5(a) an evaporated ~10 nm MoO_3 film; and 5(b) a solution processed ~10 nm MoO_3 film. Both films have been annealed at 500°C. The film coated with evaporated MoO_3 was stable until 400°C (not shown). At 500°C the evaporated MoO_3 film covering the thin metal film disintegrates forming large aggregations [5] and large apertures form in the underlying metal film [6]. At 500°C the MoO_3 film deposited by thermally converting the oxide precursor to the oxide by heating remains intact, with only very small apaertures frming in the underlying metal [7].This result shows that oxides processed from solution tend to be more effective than those that are thermally deposited.

Figure 6 shows the *JV* characteristics of organic photovoltaic devices in the dark (dotted lines) and under 1 sun illumination (solid lines) with structure: (1) 8.4 nm Au or (2) ITO electrode / TiO_2 (10 nm) / PCDTBT:$PC_{70}BM$ / WO_3 / Al. In this example the TiO_2 layer was annealed at 450°C. This example shows that an ultra-thin Au electrode can perform as well as an indium-tin oxide glass electrode when used in conjunction with a thin oxide layer that has been processed at a temperature greater than 300°C.

Figure 7 shows that if the thin metal film is patterned (e.g. with lines or apertures) the pattern is preserved at elevated temperature (500 °C) when the patterned metal film is capped with a thin oxide over layer deposited from an organometallic precursor. The figures show AFM images of a 9 nm Au film with an array of ~ 100 nm diameter apertures prepared by nanosphere lithography. The Au films are supported on a glass substrate modified with a mixed molecular adhesion layer of (3-mercaptopropyl)trimethoxysilane (MPTMS) and (3-aminopropyl)trimethoxysilane (APTMS): (a) as prepared; (b) after heating in nitrogen at 500°C for 30 minutes.; (c) after capping with a ~ 10 nm thick MoO_x over layer and heating at 500°C in nitrogen for 30 minutes (the MoO_x film was prepared by depositing an oxide precursor in the form of a solution prepared by dissolving MoO_3 in hydrogen peroxide (H_2O_2) and mixing with polyethylene glycol to adjust the concentration and viscosity. The resulting molybdenum hydroxide [possibly (MoO_2(OH)(OOH)] converts to a dense layer of MoO_x when heated. Notably the aperture size and shape of the apertures in the underlying Au film is largely preserved after heating; (d) after capping with an 10 nm thick MoO_x over layer deposited by thermal evaporation of MoO_x and heating

at 500°C for 30 minutes. The aperture size and shape has significantly deteriorated showing that deposition of the metal oxide layer directly from the metal oxide is much less effective than deposition from the metal oxide precursor.

Figure 8 shows that when a metal film is capped with a TiOx layer deposited from an organometallic precursor it is resistant to 500°C. The size and shape of apertures formed in the metal film are also preserved. The figure shows AFM images of a 9 nm Au film with an array of ~ 1 μm diameter apertures prepared by microsphere lithography. The Au films are supported on a glass substrate modified with a the molecular adhesive layer (3-aminopropyl)trimethoxysilane (APTMS): (a) as prepared; (b) the metal film is covered with an ~ 10 nm TiO_x film prepared by depositing an oxide precursor in the form of a layer of titanium (IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$) in n-butanol which converts to a dense layer of TiO_x when heated. The film with oxide was heated to 500°C for 30 minutes under nitrogen. There is no evidence of any significant change in the shape or size of the apertures. The sheet resistance remains essentially unchanged after capping with a ~ 10 nm TiO_x film overlayer and annealing to 500°C.

Figure 9 demonstrates that the process described can be applied to a different metal (namely Ag). The figure shows AFM images: (a) a 9 nm silver film supported on a glass substrate derivatised with a monolayer of (3-mercaptopropyl)trimethoxysilane. The film has been heated in a nitrogen atmosphere at 500°C for 30 minutes. The film comprises discrete islands of silver and is non-conductive.; (b) a 9 nm silver film supported on a glass substrate derivatised with a monolayer of (3-mercaptopropyl)trimethoxysilane. The metal film is covered with an ~ 10 nm TiO_x film prepared by depositing an oxide precursor in the form of a layer of titanium (IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$) in n-butanol which converts to a dense layer of TiO_x when heated. The film with oxide is heated to 500°C for 30 minutes under nitrogen. There is no evidence of Ag film disintegration. The film sheet resistance is the same as that prior to heating (~ 6 Ohms per square).

Where in this specification there is a reference to a film being "transparent", this does not imply that there is complete or substantially complete transmission of light through the film, although it may be so limited in some cases. The expression also

includes a film which is semi-transparent. The expression "transparent" encompasses a film that is optically thin, but it is not necessarily limited to a film which could be defined as optically thin.

CLAIMS

1. A method of producing a thin film structure, wherein a transparent thin film of a first metal is deposited on a substrate; there is deposited on the thin film of the first metal a compound of a second metal which forms a continuous, transparent thin film of an oxide of the second metal on the film of the first metal; and the substrate carrying the thin films is annealed at a temperature of at least about 300°C.

2. A method as claimed in claim 1, wherein the compound of a second metal that is deposited on the first metal is a precursor that is treated so as to produce the oxide of the second metal.

3. A method as claimed in claim 2, wherein the precursor comprises an organometallic compound of the second metal; or a hydroxide of the second metal; or an organometallic precursor of the oxide of the second metal, mixed with a sol of nanoparticles of the oxide of the second metal.

4. A method as claimed in claim 2 or 3, wherein the oxide precursor is deposited as a liquid.

5. A method as claimed in claim 2, 3 or 4, wherein the precursor is heated so as to produce the oxide of the second metal.

6. A method as claimed in claim 2, 3, 4 or 5, wherein the oxide of the second metal is TiO_x, WO_x, MoO_x, VO_x, TaO_x, ZnO_x, NiO_x or AlO_x.

7. A method as claimed in any preceding claim, wherein the first metal is either a single metal selected from the group consisting of gold, silver, platinum, copper, nickel, palladium, chromium, cobalt or tantalum; or an alloy of two or more metals in that group; or an alloy of one or more metals in that group, together with a metal that is not in that group; or a bilayer of a metal in that group, and another metal in that group; or a bilayer of a metal in that group and a metal that is not in that group.

8. A method as claimed in any preceding claim, wherein the film of the first metal is attached to the substrate using an adhesion layer.

9 A method as claimed in claim 8, wherein the adhesion layer is inorganic.

10. A method as claimed in claim 8, wherein the adhesion layer is a silane.

11. A method as claimed in claim 10, wherein the adhesion layer is a mixed adhesion layer of a non-amino functional silane and an aminofunctional silane.

12. A method as claimed in any preceding claim, wherein the structure is annealed at a temperature of at least about 500°C.

13. A method as claimed in any preceding claim, wherein the transparent thin film of the oxide of the second metal has a thickness of no greater than about 50 nm.

14. A method as claimed in claim 13, wherein the transparent thin film of the oxide of the second metal has a thickness of no greater than about 30 nm.

15. A method as claimed in claim 14, wherein the transparent thin film of the oxide of the second metal has a thickness of no greater than about 20 nm

16. A method as claimed in claim 15, wherein the transparent thin film of the oxide of the second metal has a thickness of no greater than about 15 nm.

17. A method as claimed in claim 16, wherein the transparent thin film of the oxide of the second metal has a thickness of no greater than about 10 nm

18. A method as claimed in any preceding claim, wherein the transparent thin film of the oxide of the second metal has a thickness of no less than about 0.5 nm.

19. A method as claimed in claim 18, wherein the transparent thin film of the oxide of the second metal has a thickness of no less than about 1 nm.

20. A method as claimed in claim 19, wherein the transparent thin film of the oxide of the second metal has a thickness of no less than about 4 nm.

21. A method as claimed in claim 20, wherein the transparent thin film of the oxide of the second metal has a thickness of no less than about 8 nm.

22. A method as claimed in any preceding claim, wherein the transparent thin film of the first metal is no more than about 20 nm thick.

23. A method as claimed in claim 22, wherein the transparent thin film of the first metal is no more than about 15 nm thick.

24. A method as claimed in claim 23, wherein the thickness of the film of the first metal is no less than about 4 nm

25. A method as claimed in claim 24, wherein the thickness of the film of the first metal is no less than about 6 nm.

26. A method as claimed in claim 25, wherein the thickness of the film of the first metal is no less than about 8 nm.

27. A method as claimed in claim 2, wherein the oxide is TiO_x which is provided by depositing a precursor in the form of a layer of titanium (IV) isopropoxide ($Ti[OCH(CH_3)_2]_4$) in n-butanol, which is converted to to a layer of TiO_x by heating.

28. A method as claimed in claim 2, wherein the oxide is MoO_x which is provided by by depositing a precursor in the form of a solution of MoO_x in hydrogen peroxide (H_2O_2) which is converted to layer of MoO_x by heating.

29. A method as claimed in claim 2, wherein the oxide is ZnOx which is prepared by depositing a precursor in the form of a solution of zinc acetate dihydrate and ethanolamine in alcohol, which is converted to ZnO_x by heating.

30. A method as claimed in claim 2, wherein the oxide is WOx which is prepared by depositing a precursor in the form of a solution of Tungsten(VI) Isopropoxide, which is converted to WOx by heating.

31. A method as claimed in claim 2, wherein the oxide is VOx which is prepared by depositing a precursor in the form of an isopropanol solution of vanadium(V) oxitriisopropoxide, and heating.

32. A method as claimed in claim 2, wherein the oxide is ZrOx which is prepared by depositing a precursor in the form of a solution of zirconium oxychloride ($ZrOCl_2$) mixed with 2-methoxyethanol and H_2O_2 and heating.

33. A method as claimed in claim 2, wherein the oxide is AlOx which is prepared by depositing a precursor in the form of $AlCl_3$ in a solvent of acetonitrile with ethylene glycol, and heating.

34. A method as claimed in any preceding claim, wherein the substrate is transparent.

35. A method as claimed in claim 34, wherein the structure is in the form of a transparent electrode.

36. A thin film semiconductor device comprising a transparent electrode produced by a method as claimed in claim 35, a donor semiconductor material, an acceptor semiconductor material, and a second electrode.

37. A semiconductor device as claimed in claim 36, wherein at least one of the semiconductor materials is an organic semiconductor material.

38. A semiconductor device as claimed in claim 37, in the form of an organic photovoltaic device.

39. A semiconductor device as claimed in claim 36, in the form of a dye sensitised photovoltaic device.

40. A thin film semiconductor device comprising a transparent electrode produced by a method as claimed in claim 35, an n-type semiconductor material, a p-type semiconductor material, and a second electrode.

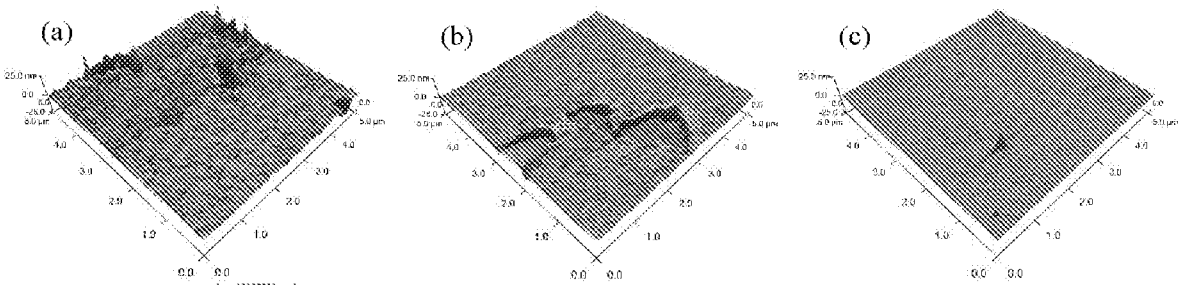


Figure 1

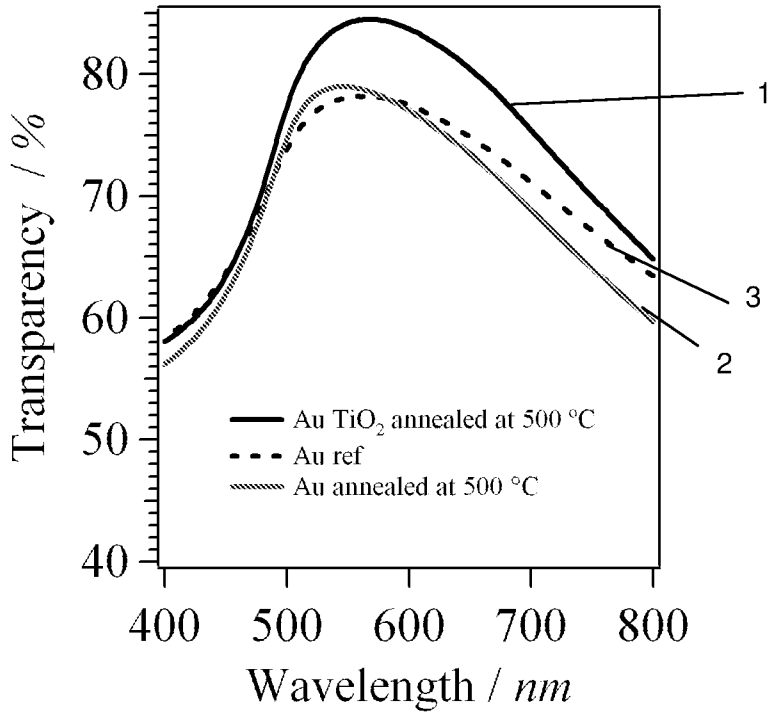
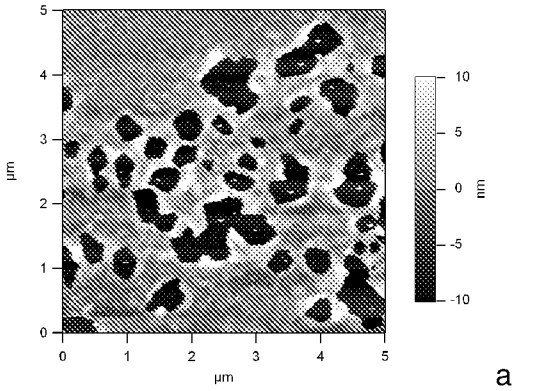


Figure 2



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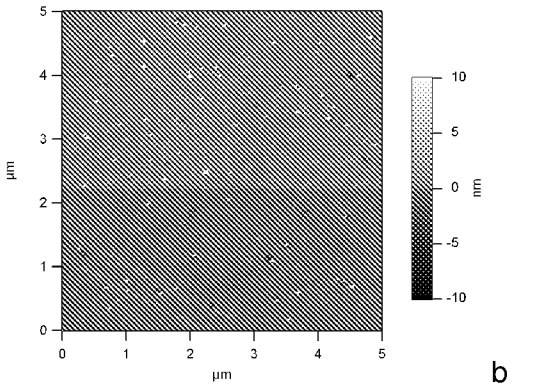

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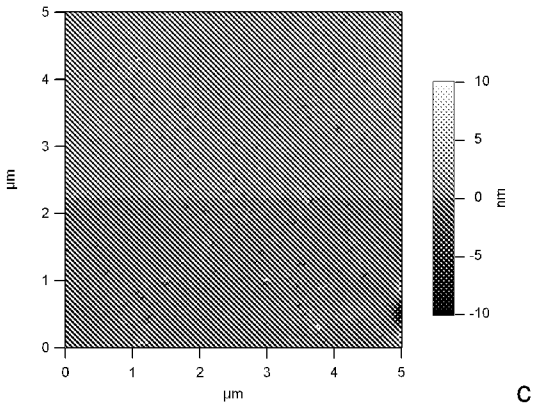
Figure 3



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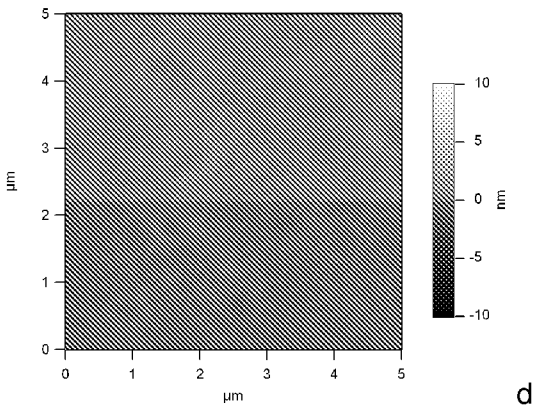
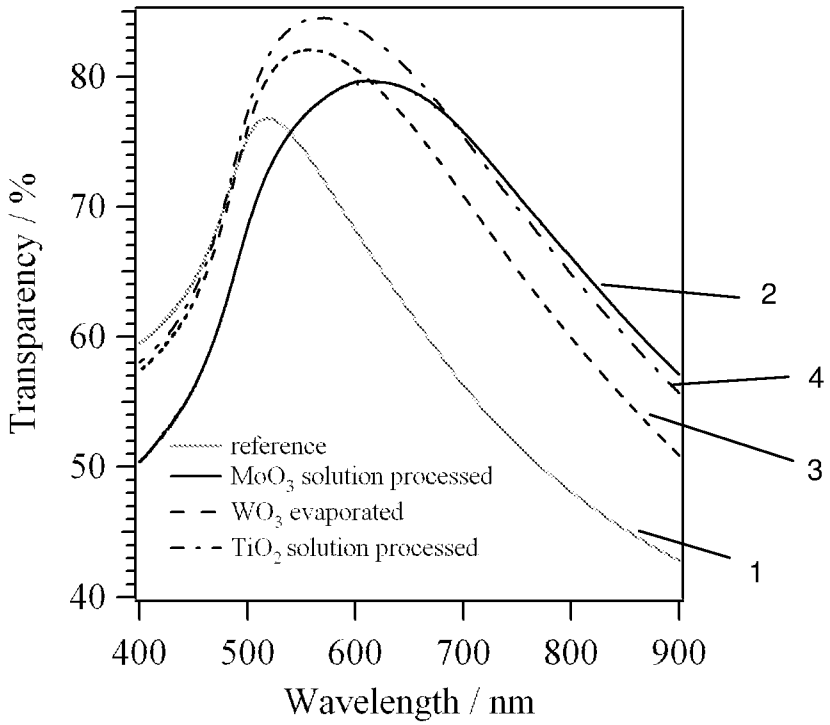


d

Figure 4



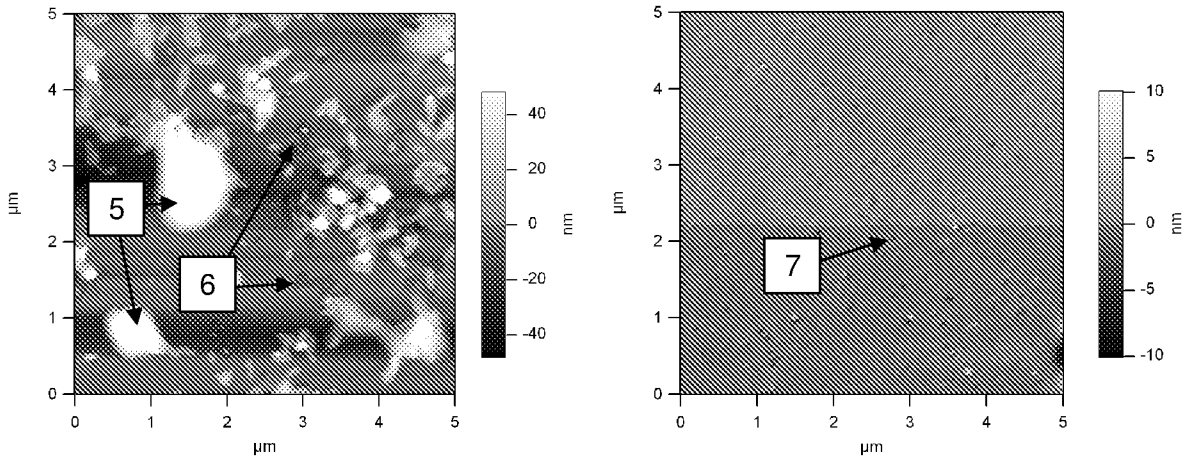


Figure 5

Figure 6

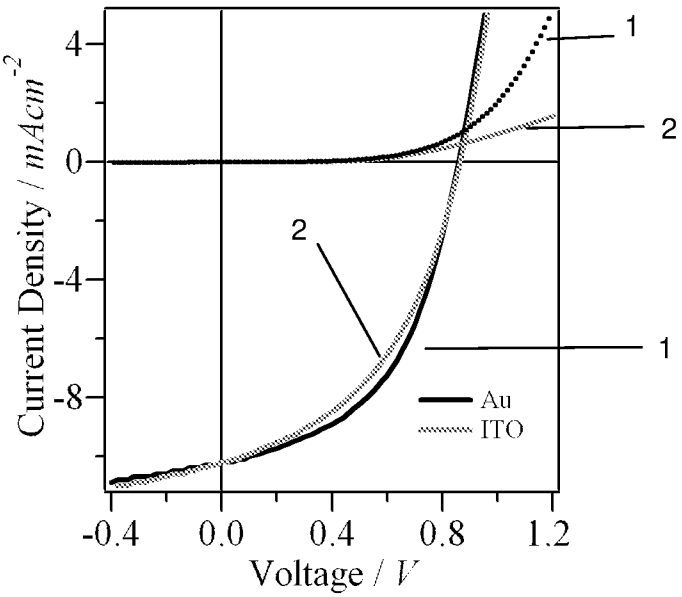
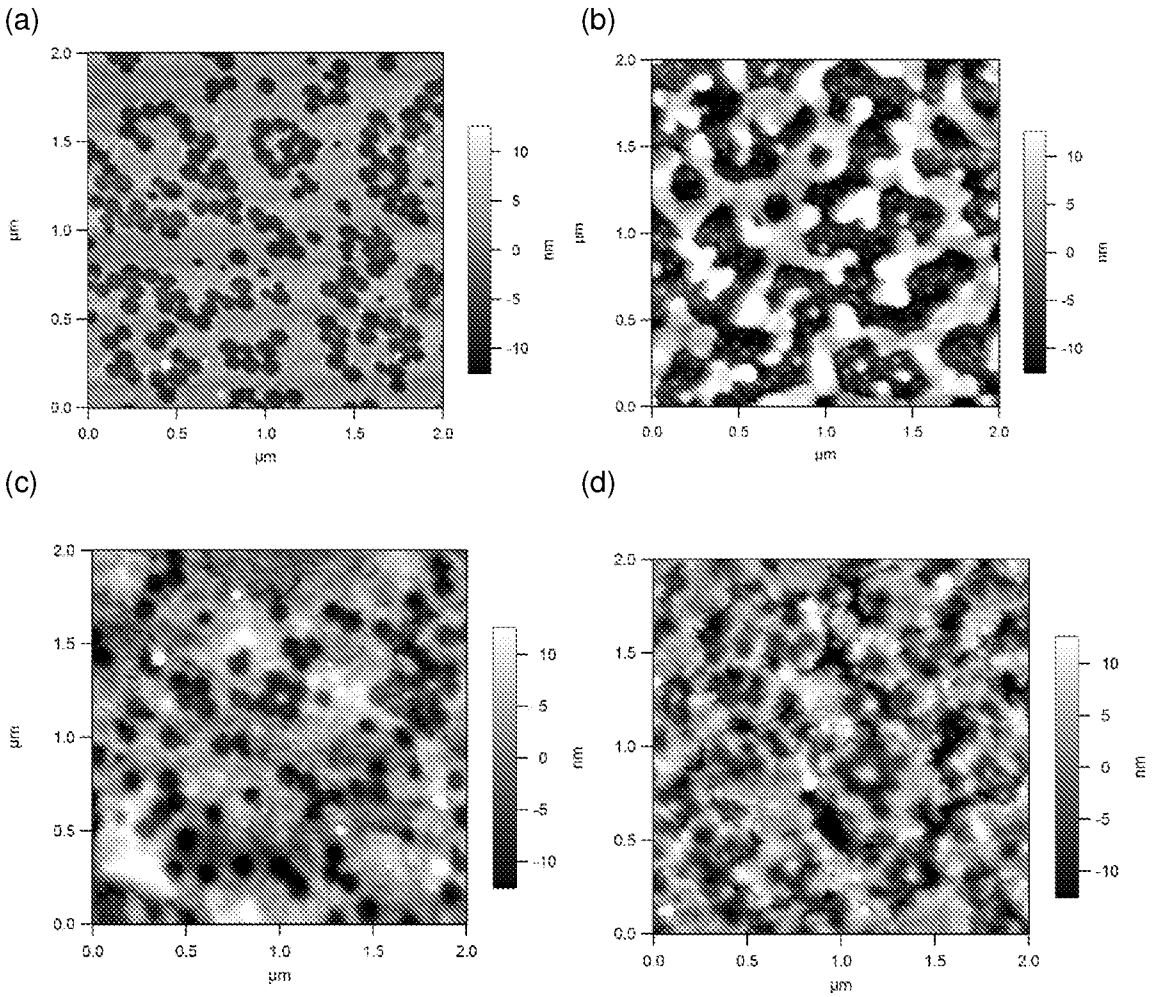


Figure 7



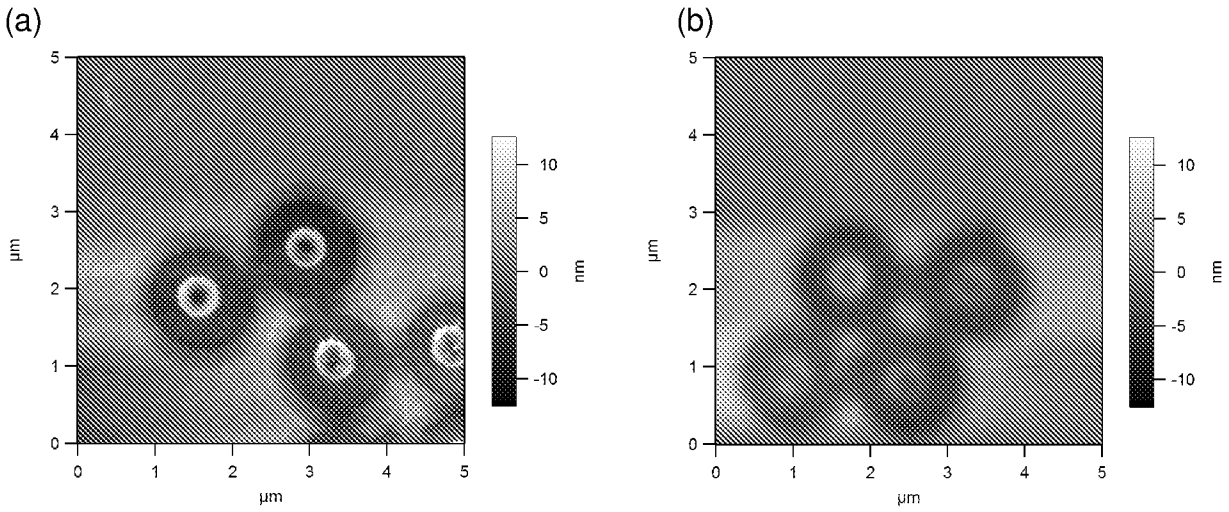


Figure 8

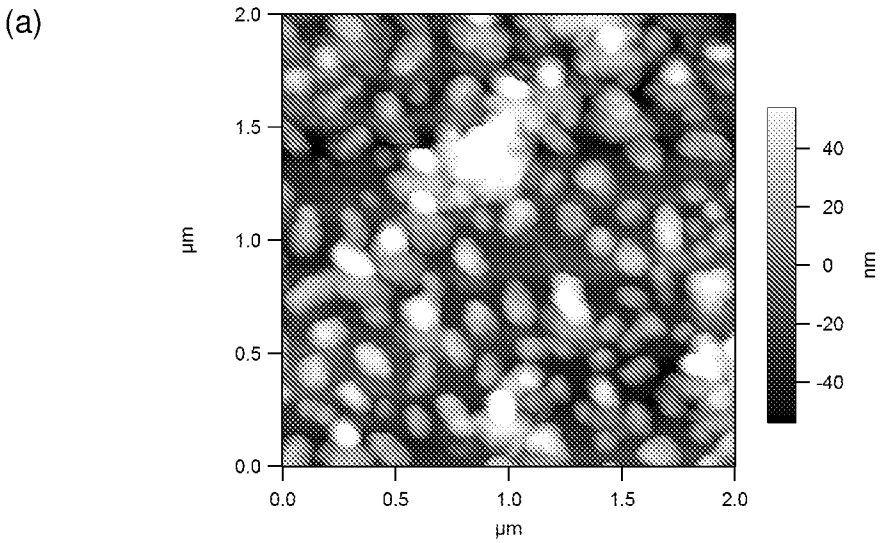


Figure 9