



(51) International Patent Classification:

C03C 17/10 (2006.01) C03C 17/25 (2006.01)  
C23C 18/12 (2006.01)

(21) International Application Number:

PCT/GB2017/050296

(22) International Filing Date:

6 February 2017 (06.02.2017)

(25) Filing Language:

English

(26) Publication Language:

English

(30) Priority Data:

1602083.6 5 February 2016 (05.02.2016) GB

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AO, AT, AU, AZ, BA, BB, BG, BH, BN, BR, BW, BY, BZ, CA, CH, CL, CN, CO, CR, CU, CZ, DE, DJ, DK, DM, DO, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, GT, HN, HR, HU, ID, IL, IN, IR, IS, JP, KE, KG, KH, KN, KP, KR, KW, KZ, LA, LC, LK, LR, LS, LU, LY, MA, MD, ME, MG, MK, MN, MW, MX, MY, MZ, NA, NG, NI, NO, NZ, OM, PA, PE, PG, PH, PL, PT, QA, RO, RS, RU, RW, SA, SC, SD, SE, SG, SK, SL, SM, ST, SV, SY, TH, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU,

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(54) Title: METAL OXIDE FILM

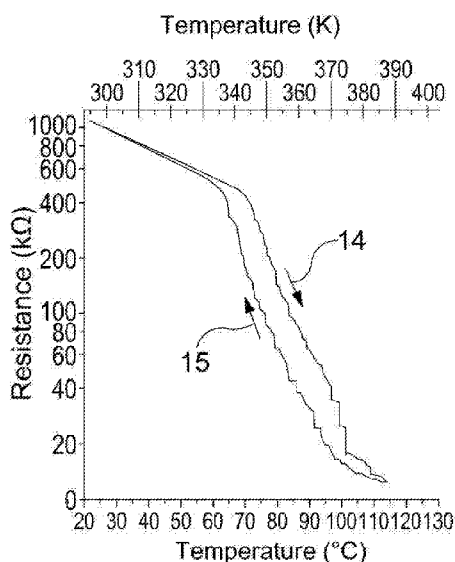


Figure 4

(57) Abstract: A process for producing a metal oxide film comprising: providing a precursor solution or dispersion containing a metal complex; spraying the precursor solution on to a heated substrate in the presence of water, thereby depositing material on the substrate; and drying the deposited material, thereby producing the metal oxide film.

TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, **Published:**  
DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, — *with international search report (Art. 21(3))*  
LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE,  
SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA,  
GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

## Metal Oxide Film

The invention relates to a process for producing a metal oxide film, to metal oxide films obtainable or obtained by that process, to various uses of such metal oxide films, and to products comprising such metal oxide films. The metal oxide films may  
5 comprise, or consist essentially of, undoped or doped metal oxide.

Thermochromic materials are characterised by a semiconductor-to-metal transition, which occurs due to a reversible change in the materials' crystalline and/or electronic  
10 structure as a function of temperature. Changes in the materials' optical, electrical and magnetic properties occur as a result of the semiconductor-to-metal transition.

Thermochromic materials are of interest because they have several potentially useful applications, including for instance in smart windows, through which light and heat  
15 transmittance varies according to the surrounding or ambient temperature. Such smart windows may be particularly useful in thermal management of buildings in hot areas of the world.

Vanadium (IV) oxide ( $\text{VO}_2$ ) is a particularly interesting thermochromic material, e.g.  
20 for use in smart windows, because it exhibits a large reversible change in its optical, electrical and magnetic properties caused by a semiconductor-to-metal transition at temperatures around  $70^\circ\text{C}$ . The temperature at which the semiconductor-to-metal transition occurs can be modified by chemical doping. For instance, doping  $\text{VO}_2$  with high-valent transition metals such as niobium, molybdenum or tungsten reduces the  
25 temperature at which the semiconductor-to-metal transition occurs. On the other hand, doping  $\text{VO}_2$  with trivalent cations such as chromium and aluminium increases the temperature at which the semiconductor-to-metal transition occurs.

However, to date, a reliable, scalable, cost-effective and energy-efficient process for  
30 producing undoped or doped  $\text{VO}_2$  films has not been developed. The lack of such a process is holding back the development and commercialisation of products such as smart windows which could make use of  $\text{VO}_2$ 's unique properties.

The chemistry of vanadium oxides is one reason why it is difficult to produce  $\text{VO}_2$   
35 films of good purity (e.g. with a purity of 90% or more). Vanadium can have several

oxidation states and hence can form several oxides, each with significantly different magnetic and electrical properties. Edwards P., Kuznetsov V., Slocombe D. and Vijayaraghavan R. The Electronic Structure and Properties of Solids. In: Jan Reedijk and Kenneth Poeppelmeier, editors. Comprehensive Inorganic Chemistry II, Vol 4. Oxford: Elsevier; 2013. p. 153-176 discusses the electronic structure and properties of solids, in particular oxides.

Attempts have been made to produce VO<sub>2</sub> films by liquid-feed flame spray reaction processes (pyrolysis). However, the results have generally been unsatisfactory, since the films produced have not had good purity. Without wishing to be bound by any theory, this could be due to the flame being too hot and the fact that the flame pyrolysis process is run in air. US2006/0165898 discloses efforts to decrease the flame temperature by contacting the flame with a cooling medium.

Hydrothermal routes for producing VO<sub>2</sub> films have also proved unsatisfactory. The above-atmospheric pressures involved dictate that such processes can be expensive and/or subject to a relatively high risk-element. Furthermore, such hydrothermal routes do not offer a readily scalable process for producing VO<sub>2</sub> films of high purity.

R. Binions et al., *J. Mater. Chem.*, 2007, 17, 4652-4660 describes the preparation of VO<sub>2</sub> thin films by atmospheric pressure chemical vapour deposition (APCVD) from vanadyl acetylacetonate and tungsten hexachloride.

B. W. Mwakikunga et al., *Optical Materials* 29 (2007) 481-487 describes the production of sub-micrometre structured VO<sub>2</sub> thin films by ultrasonic nebula-spray pyrolysis from the precursor vanadium trichloride in an aqueous solution of 0.085 M ammonium meta-vanadate.

US4,100,330 discloses a method for coating a glass substrate with a first film of silicon and a second film of metal oxide by pyrolytic coating techniques. The method involves maintaining the glass surface at a temperature of at least about 400°C and contacting the hot glass surface first with a silane-containing gas in a non-oxidizing atmosphere to form a silicon film and second with a solution of an organometallic coating compound in an oxidizing atmosphere to form a metal oxide film.

US4,240,816 discloses a method and apparatus for filming and tempering a pre-cut glass sheet in a continuous process.

US4,125,391 discloses a process for forming a metal or metal compound coating on a face of a glass substrate by contacting such face while it is at elevated temperature with droplets comprising a metal compound which by pyrolysis forms the coating metal or metal compound on the face.

A first aspect of the invention provides a process for producing a metal oxide film comprising:

providing a precursor solution or dispersion containing a metal complex;  
spraying the precursor solution on to a heated substrate in the presence of water, thereby depositing material on the substrate; and  
drying the deposited material, thereby producing the metal oxide film.

15

The invention provides a spray pyrolytic process for the preparation of doped and undoped metal oxide, e.g. vanadium (IV) oxide, films.

In an embodiment, the precursor solution may be an aqueous solution. The precursor solution may comprise an aqueous solvent mixture or an aqueous/non-aqueous solvent mixture.

20

The concentration of the precursor solution may be up to 0.1M. The concentration of the precursor solution may be up to 0.05M.

25

One or more phases of the metal oxide may be present in the metal oxide film.

The metal oxide film may comprise, or consist essentially of, a metal (IV) oxide film ( $\text{MO}_2$ , where M is a metal). The metal oxide film may comprise, or consist essentially of, vanadium (IV) oxide.

30

The metal oxide film may comprise, or consist essentially of, a metal (III) oxide film ( $\text{M}_2\text{O}_3$ ), where M is a metal). For instance, the metal oxide film may comprise, or consist essentially of, vanadium (III) oxide ( $\text{V}_2\text{O}_3$ ).

35

The metal, M, may comprise vanadium, molybdenum, tungsten, germanium or manganese. Accordingly, the metal complex may be a vanadium complex, a molybdenum complex, a tungsten complex, a germanium complex or a manganese complex. For instance, the metal complex may be a vanadium (III) complex, a  
5 vanadium (IV) complex, a molybdenum (IV) complex, a molybdenum (VI) complex, a molybdenum (VIII) complex, a tungsten (IV) complex, a germanium (IV) complex or a manganese (IV) complex.

The metal complex may comprise one or more ligands. The ligand(s) may comprise a  
10 diketone such as acetylacetonate (acac). The ligand(s) may comprise oxalate (ox). Other suitable ligands may include simple carboxylic acids, amino acids, alpha-hydroxy carboxylic acids, citrates, beta-keto esters and beta-keto iminates.

Selecting a given ligand can affect the purity of the metal oxide powder produced by  
15 the process. The structure of the ligand is crucial to determining the temperature of decomposition of the metal complex and consequently the purity of the metal oxide film.

Advantageously, the process may produce metal oxide films, e.g. vanadium (IV) oxide  
20 films, of very good purity (e.g. with a purity of 90% or more).

In an embodiment, the oxidation state of the metal may be the same in the metal complex as it is in the metal oxide film.

25 In some embodiments, importantly, the metal does not change oxidation state during the spray pyrolysis process, i.e. it exists in the same oxidation state in the precursor complex as in the final film product. Without wishing to be bound by any theory, it is thought that this results in the metal oxide film produced in accordance with the invention being of very good purity (i.e. at least 90% pure).

30

The vanadium complex, e.g. the vanadium (IV) complex, may comprise a vanadyl ion ( $\text{VO}^{2+}$ ) and one or more ligands. Vanadyl acetylacetonate  $[\text{VO}(\text{acac})_2]$  may be a suitable vanadium (IV) complex. Vanadyl oxalate  $[\text{VO}(\text{ox})]$ , e.g.  $[\text{VO}(\text{ox})(\text{H}_2\text{O})_2]$  or  $[\text{VO}(\text{ox})_2]^{2-}$ , may be a suitable vanadium (IV) complex.

35

Advantageously, vanadyl acetylacetonate is sufficiently water soluble for use in the process of the invention. However, a more water soluble vanadium complex, e.g. vanadium (IV) complex, may be more preferable.

5 Advantageously, vanadyl oxalate has better solubility in water. Another benefit of vanadyl oxalate is that the precursor materials, e.g. oxalic acid, typically may be relatively inexpensive. In addition, VO<sub>2</sub> films produced using vanadyl oxalate as the vanadium complex have been found typically to be cleaner than VO<sub>2</sub> films produced using vanadyl acetylacetonate as the vanadium complex.

10

The molybdenum complex may comprise a molybdenyl ion (MoO<sub>2</sub><sup>2+</sup>) and one or more ligands. Molybdenyl acetylacetonate [MoO<sub>2</sub>(acac)<sub>2</sub>], a molybdenum (VI) complex, may be a suitable molybdenum complex. Molybdenyl oxalate [MoO<sub>2</sub>(ox)<sub>2</sub>], a molybdenum (VIII) complex, may be a suitable molybdenum complex. A molybdenum (IV) complex comprising

15 suitable ligands may be a suitable molybdenum complex.

Advantageously, use of a water-soluble metal complex may be preferred, since it may then be safer and easier to practise the invention.

20 In an embodiment, the precursor solution may comprise a solution of the metal complex, e.g. vanadium complex or molybdenum complex, in an aqueous solvent mixture. The aqueous solvent mixture may comprise an alcohol, e.g. ethanol, and water. In addition, the precursor solution may further comprise an acid, e.g. acetic acid. Additionally or alternatively, the precursor solution may comprise a ketone such

25 as acetone.

In an embodiment, the precursor solution may comprise 0.228M vanadyl acetylacetonate [VO(acac)<sub>2</sub>] in a 2:1 by volume mixture of ethanol to 7% by volume acetic acid in water.

30

In an embodiment, the precursor solution may comprise vanadyl oxalate [VO(ox)]. The precursor solution may be an aqueous solution. The precursor solution may comprise acetone.

In an embodiment, the precursor solution may comprise one or more further metals, e.g. zinc, chromium, aluminium, niobium, molybdenum (when not producing a molybdenum oxide) and/or tungsten (when not producing a tungsten oxide), as dopants. Accordingly, the metal oxide film, e.g. vanadium (IV) oxide film, produced  
5 by the process may comprise, or consist essentially of, undoped metal oxide or doped metal oxide.

A precursor solution containing the dopant(s) may be supplied to a nozzle and sprayed on to the heated substrate. Alternatively or additionally, the dopant(s) may be  
10 supplied to a nozzle separately from the precursor solution or dispersion containing the metal complex; the dopant(s) may then be mixed with the precursor solution or dispersion containing the metal complex at the nozzle immediately before spraying. Alternatively or additionally, one or more solutions or dispersions containing the  
15 dopant(s) may be sprayed from one or more different nozzles from the precursor solution or dispersion containing the metal complex, such that the solutions or dispersions mix together as they are sprayed on to the substrate.

The amount of the dopant(s) may be varied during spraying of the precursor solution on to the heated substrate. By controlling the flow rate of a suspension or dispersion  
20 containing the dopant(s) to the nozzle(s) relative to the flow rate of the precursor solution or dispersion containing the metal complex, the amount of the dopant(s) may be varied without stopping the spraying of the precursor solution on to the heated substrate.

25 Suitable precursor materials for the dopant(s) may include water-soluble metal salts, e.g. a water-soluble zinc, chromium, aluminium, niobium, molybdenum (when not producing a molybdenum oxide) and/or tungsten (when not producing a tungsten oxide) salt.

30 In an embodiment, the precursor solution or dispersion may be sprayed on to the heated substrate in a controlled and/or a protective and/or an inert atmosphere, e.g. nitrogen. Typically, the precursor solution may be sprayed on to the heated substrate in an atmosphere other than air.



In an embodiment, the precursor solution or dispersion may be sprayed on to the heated substrate with the aid of a carrier gas. Typically, the carrier gas may be non-reactive; for instance, the carrier gas may comprise, or consist essentially of, nitrogen.

- 5 In an embodiment, the precursor solution or dispersion may be sprayed on to the heated substrate in a humid atmosphere. For example, the humid atmosphere may be provided by a water-containing (e.g. water-saturated) carrier gas, e.g. water-saturated nitrogen, and/or water in the precursor solution.
- 10 In an embodiment, the precursor solution or dispersion may be sprayed on to the heated substrate at a rate of up to 5 ml/min. The precursor solution may be sprayed on to the heated substrate at a rate of at least 0.2 ml/min. For example, the precursor solution or dispersion may be sprayed on to the heated substrate at a rate of at least 0.5 ml/min and/or up to 3 ml/min. The precursor solution or dispersion may be
- 15 sprayed on to the heated substrate at a rate of 1 ml/min.

In an embodiment, the carrier gas may be sprayed at a rate of at least 4 ml/min and/or up to 60 ml/min. The carrier gas may be sprayed at a rate of up to or at least 7 ml/min and/or up to or at least 15 ml/min.

20

The rate at which the precursor solution or dispersion is sprayed and/or the rate at which the carrier gas is sprayed may be substantially constant or may be varied.

- In an embodiment, the substrate may be heated to a temperature of at least 150°C, at
- 25 least 175°C, at least 300°C, at least 400°C, at least 450°C and/or up to 550°C. The substrate may be heated to a temperature of at least 460°C and/or up to 530°C. For instance, the substrate may be heated to a temperature of approximately 460°C, 490°C or 530°C.

- 30 During spraying of the precursor solution, the substrate may be held at a substantially constant temperature or the temperature of the substrate may be varied.

- In an embodiment, the process may comprise the step of, before spraying the precursor solution, heating the substrate. The substrate may be heated at a rate of up
- 35 to or at least 30°C/min.

In an embodiment, drying the deposited material may be carried out in a controlled and/or a protective and/or an inert atmosphere, e.g. nitrogen.

Carrying out the spraying, and typically the drying, steps in an inert atmosphere may be beneficial, in that it may prevent the generation of higher oxidation states. Thus, for example, high quality vanadium (IV) oxide films can be formed in accordance with the present invention. In contrast, in prior art processes carried out in air, typically higher, e.g. the highest possible, oxidation states will be formed.

In an embodiment, drying the deposited material may comprise maintaining the substrate at a predetermined drying temperature for a predetermined drying time.

The predetermined drying temperature may be substantially constant or may vary during the drying of the deposited material.

15

Conveniently, the predetermined drying temperature may be the same as the temperature to which the substrate is heated during spraying of the precursor solution on to the heated substrate. For instance, the predetermined drying temperature may be at least 150°C, at least 175°C, at least 300°C, at least 400°C, at least 450°C and/or up to 550°C. The predetermined drying temperature may be at least 460°C and/or up to 530°C. For instance, the predetermined drying temperature may be approximately 460°C, 490°C or 530°C.

20

The predetermined drying time may be at least 5 minutes and/or up to 60 minutes.

The predetermined drying time may be approximately 30 minutes or approximately 40 minutes.

25

In an embodiment, the method may comprise heat treating, e.g. annealing, the deposited material. For instance, the heat treatment, e.g. annealing, may be carried out at a predetermined annealing temperature for a predetermined annealing time. The heat treatment, e.g. annealing, may be carried out in an inert atmosphere, e.g. a nitrogen atmosphere.

30

Conveniently, the predetermined annealing temperature may be the same as, or similar to, the temperature to which the substrate is heated during spraying of the precursor

35

solution on to the heated substrate. For instance, the predetermined annealing temperature may be at least 300°C, at least 400°C, at least 450°C and/or up to 550°C. The predetermined annealing temperature may be at least 460°C and/or up to 530°C. For instance, the predetermined annealing temperature may be approximately 460°C,  
5 490°C, 525°C or 530°C.

The predetermined annealing time may be up to or at least 60 minutes, up to or at least two hours or up to or at least 3 hours. For instance, the predetermined annealing time time may be approximately three hours.

10

In an embodiment, the steps of spraying the precursor solution on to a heated substrate in the presence of water, thereby depositing material on the substrate and drying the deposited material may be repeated one or more times, e.g. at regular intervals. For instance, the step of spraying the precursor solution on to a heated substrate in the  
15 presence of water, thereby depositing material on the substrate may be repeated at intervals of up to or at least 5 minutes, up to or at least 10 minutes, up to or at least 15 minutes, up to or at least 20 minutes, and/or up to or at least 30 minutes.

In an embodiment, the process may comprise the step of, after drying (for the last  
20 time), cooling the deposited material on the substrate. The deposited material on the substrate may be cooled in a controlled and/or a protective and/or an inert atmosphere, e.g. nitrogen.

The deposited material on the substrate may be cooled at a controlled cooling rate.

25

The controlled cooling rate may be substantially constant or may vary during the cooling of the deposited material on the substrate.

Typically, the controlled cooling rate may be relatively rapid. The controlled cooling  
30 rate may be at least 10°C/min or at least 15°C/min. For instance, the controlled cooling rate may be approximately 15°C/min, approximately 25°C/min or approximately 40°C/min.

It has been found that pH has an effect on the performance of the process.  
35 Accordingly, the process may work particularly well when the pH is controlled such

that it is within a preferred operating pH range. The preferred operating pH range will depend on the choice of precursor complex and/or solution and/or other operating conditions, e.g. temperature. Generally, if the pH is too alkaline, then unwanted precipitates may form; if the pH is too acidic, then the metal oxide may not form a film on the substrate. Typically, the preferred pH operating range may be between 5 and 9. In an embodiment, the pH of the precursor solution may be at least 5 and/or up to 9. The pH of the precursor solution may be at least 5.5 or at least 6. The pH of the precursor solution may be up to 8.5 or up to 8.

10 In an embodiment, the process may comprise a step of preparing the precursor solution. The precursor solution may be prepared 48 hours or less before being sprayed on to the heated substrate.

In an embodiment, the precursor solution may be prepared by dissolving  $V_2O_5$  and oxalic acid in water. The precursor solution may be warmed to facilitate dissolution of the  $V_2O_5$  and oxalic acid. The precursor solution may include acetone.

In an embodiment, the substrate may comprise, or consist essentially of, a glass, e.g. a silicate glass such as soda-lime glass. The substrate may be made at least partially from materials other than glasses, e.g. non-vitreous materials.

The substrate may be of any suitable size and/or shape. For instance, the substrate may or may not be flat.

25 The substrate may be stationary or moving, e.g. while the precursor solution is being sprayed on to the substrate. For instance, the substrate may move relative to a coating apparatus comprising one or more nozzle(s) operable to spray the precursor solution on to the substrate.

30 Films manufactured in accordance with the invention may be used to coat windows for buildings or vehicles, e.g. aerospace vehicles. Additionally or alternatively, such films may be used as infra-red absorbing coatings. Such films may also have utility in holographic and data storage applications, e.g. in ultra-fast optical or electrical switching devices.

Advantageously, the process may be carried out in-line with a float glass manufacturing process. Consequently, the process may be part of a substantially continuous manufacturing process for producing smart windows for buildings or vehicles.

5

In an embodiment, the substrate may comprise a ribbon of float glass. In embodiments in which the substrate moves, the ribbon of float glass may be continuous.

10 In the float glass process, glass floats on a bath of molten metal, e.g. tin, as it solidifies.

Accordingly, the glass will be at an elevated temperature as it floats on the bath of molten metal. An appropriate point on the float glass production line may be selected  
15 for carrying out the process of the invention, since the temperature of the glass may generally be known at each point along the production line.

In another aspect, the invention provides a product comprising a substrate with a film thereon, the film comprising or consisting essentially of a metal oxide film obtained  
20 or obtainable by the process of the first aspect of the invention.

In another aspect, the invention provides the use of a product comprising a substrate with a film thereon, the film comprising or consisting essentially of a metal oxide film obtained or obtainable by the process of the first aspect of the invention.

25

In order that the invention may be well understood, it will now be described with reference to the accompanying drawings, in which:

Figure 1 shows the typical variation of electrical resistance with temperature for a  
30 deposited VO<sub>2</sub> film;

Figure 2 shows the typical variation of optical transmittance of VO<sub>2</sub> deposited as a film at 2500 nm as a function of temperature;

Figure 3 is a scanning electron microscope (SEM) image of VO<sub>2</sub> deposited as a film in accordance with the invention;

Figure 4 shows the variation of electrical resistance with temperature for the VO<sub>2</sub> film shown in Figure 3;

Figure 5 is an x-ray diffraction (XRD) spectrum for the VO<sub>2</sub> film shown in Figure 3;

Figure 6 is an XRD spectrum for another example embodiment of VO<sub>2</sub> deposited as a film in accordance with the invention; and

Figure 7 is an XRD spectrum for another example embodiment of VO<sub>2</sub> deposited as a film in accordance with the invention.

Figure 1 shows the typical variation of electrical resistance with temperature for deposited VO<sub>2</sub> film. As can be seen in Figure 1, there is a step-change in electrical resistance at around 60°C to 70°C. The step-change in electrical resistance is approximately two orders of magnitude. This change in electrical resistance is a consequence of the semiconductor-to-metal transition. As can be seen in Figure 1, the typical variation of electrical resistance with temperature for the VO<sub>2</sub> film has a hysteresis of around 15°C in width. In Figure 1, one of a series of data points for heating is labelled 1 and one of a series of data points for cooling is labelled 2.

Figure 2 shows the typical variation of optical transmittance of VO<sub>2</sub> deposited as a film at 2500 nm wavelength as a function of temperature. As can be seen in Figure 2, there is a significant change in optical transmittance at around 60°C to 70°C. This change in optical transmittance is a consequence of the semiconductor-to-metal transition. At temperatures above the transition, the optical transmittance of the VO<sub>2</sub> film at 2500 nm is between 30% and 40%; at temperatures below the transition, the optical transmittance of the VO<sub>2</sub> film at 2500 nm is around 90%. As can be seen in Figure 2, the typical variation of optical transmittance of VO<sub>2</sub> deposited as a film at 2500 nm as a function of temperature has a hysteresis of around 15°C in width. In Figure 2, one of a series of data points for heating is labelled 3 and one of a series of data points for cooling is labelled 4.

Thus, the optical transmittance of VO<sub>2</sub> deposited as a film changes significantly, due to the semiconductor-to-metal transition. At temperatures below the transition, VO<sub>2</sub> films are substantially transparent. At temperatures above the transition, VO<sub>2</sub> films are significantly less transparent (more opaque). In VO<sub>2</sub>, the semiconductor-to-metal transition occurs at around 70°C. This is not that much higher than the temperatures that can be reached on hot days in some parts of the world. It is this change in optical

properties and the temperature at which the change occurs, which makes the use of doped or updoped VO<sub>2</sub> films of particular interest in the manufacture of smart windows.

In accordance with the invention, spray pyrolysis can be used to deposit VO<sub>2</sub> as a film  
5 on a substrate.

Several experiments were conducted, in order to determine suitable conditions for reliably producing VO<sub>2</sub> films by spray pyrolysis.

10 Generally, the process involves providing a precursor solution containing a vanadium (IV) complex. The precursor solution is then sprayed in the presence of water on to a heated substrate, thereby depositing material on the substrate. After spraying, the deposited material is dried by maintaining the substrate at a predetermined drying temperature for a predetermined drying time. After drying, the deposited material on  
15 the substrate is cooled to ambient temperature at a controlled, relatively quick, rate.

X-ray diffraction (XRD) data from VO<sub>2</sub> films successfully produced by spray pyrolysis in accordance with the invention indicate two main phases: V<sub>3</sub>O<sub>5</sub> (an oxygen-deficient semiconducting phase and VO<sub>2</sub> in its low-temperature M1  
20 monoclinic form. Typically, there is a peak in the XRD spectra at 9° and peaks at 30°. The peak at 9° is associated with V<sub>3</sub>O<sub>5</sub>; the peaks at 30° are associated with V<sub>3</sub>O<sub>5</sub> and VO<sub>2</sub>. In some instances, the peak at 9° was more intense than the peaks at 30°; in other instances, the peaks at 30° were stronger.

25 Table 1 below shows spray pyrolysis conditions that were found by the applicant to produce good quality VO<sub>2</sub> films (A-K) on a glass substrate. The films were around 300 nm thick.

Film	Substrate temp. (°C)	Carrier gas	Cooling rate (°C/min)	Drying time (mins)	Precursor complex	Precursor solution conc. (M)	Carrier gas flow rate (ml/min)	Precursor solution spray rate (ml/min)
A	530	N <sub>2</sub>	15	60	[VO(acac) <sub>2</sub> ]	0.05	7	0.5
B	530	N <sub>2</sub>	15	60	[VO(acac) <sub>2</sub> ]	0.0228	15	1
C	530	N <sub>2</sub>	15	45	[VO(acac) <sub>2</sub> ]	0.0228	15	1
D	530	N <sub>2</sub>	15	60	[VO(acac) <sub>2</sub> ]	0.0228	15	1

E	530	N <sub>2</sub>	15	5	[VO(acac) <sub>2</sub> ]	0.0228	15	1
F	530	N <sub>2</sub>	15	30	[VO(acac) <sub>2</sub> ]	0.0228	15	1
G	530	N <sub>2</sub>	15	30	[VO(acac) <sub>2</sub> ]	0.0228	15	1
H	530	N <sub>2</sub>	40	30	[VO(acac) <sub>2</sub> ]	0.0228	15	1
I	465	N <sub>2</sub>	15	30	[VO(acac) <sub>2</sub> ]	0.0228	15	1
J	490	N <sub>2</sub>	15	30	[VO(acac) <sub>2</sub> ]	0.0228	15	1
K	530	N <sub>2</sub>	15	30	[VO(acac) <sub>2</sub> ], with 2 mol% [Zn(acac) <sub>2</sub> .H <sub>2</sub> O]	0.0228	15	1

Table 1

The spray pyrolysis conditions and parameters used to produce film A successfully produced a uniform film. A hysteresis typical of the semiconductor-to-metal transition in VO<sub>2</sub> was seen in measurements of the variation of electrical resistance with temperature for film A.

In producing film B, the effects of carrier gas flow rate, precursor solution spray rate and precursor solution concentration on the reliability of film production were tested. A hysteresis typical of the semiconductor-to-metal transition in VO<sub>2</sub> was seen in measurements of the variation of electrical resistance with temperature for film B.

Film C was produced using the same conditions and parameters as film B, except that the drying time was shorter (45 minutes instead of 60 minutes). A hysteresis typical of the semiconductor-to-metal transition in VO<sub>2</sub> was seen in measurements of the variation of electrical resistance with temperature for film C.

Figure 3 is a scanning electron microscope (SEM) image of film D. The image was taken using an accelerating voltage of 5 kV and at a working distance of 10 mm. The magnification of the SEM image is 50000 times.

Figure 4 shows the variation of electrical resistance with temperature for film D. A hysteresis typical of the semiconductor-to-metal transition in VO<sub>2</sub> can be seen. An arrow labelled 14 indicates heating; an arrow labelled 15 indicates cooling.

25

Figure 5 is an x-ray diffraction (XRD) spectrum of film D. The spectrum contains a prominent peak 16 at around 9° and smaller, significant peaks 17 at around 30°.



Film D was produced under the same spray pyrolysis conditions as film B. This was done to test the reproducibility of the process used to produce film B. The successful production of film D indicated that the process used to produce film B was reproducible.

5

Film E appeared to be a normal-looking VO<sub>2</sub> film produced in accordance with the invention. In producing the film E, a very short drying time was used (5 minutes). No significant hysteresis loop was seen in measurements of the variation of electrical resistance with temperature for film E. Without wishing to be bound by any theory, the absence of a significant hysteresis loop for film E could be a consequence of the very short drying time used in producing the film E. The other spray pyrolysis conditions used in the production of film E were the same as were used in the production of films B and D, both of which exhibited an observable, significant hysteresis loop in the variation of electrical resistance with temperature.

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A hysteresis typical of the semiconductor-to-metal transition in VO<sub>2</sub> was seen in measurements of the variation of electrical resistance with temperature for film F and film G.

20 Films F and G were produced using the same spray pyrolysis process conditions. This suggests that the practising the process using these process conditions produces reproducible results in terms of film production.

The process for producing film H was successful in that it produced a good VO<sub>2</sub> film. 25 The process conditions included a relatively fast cooling rate of 40°C/min. A hysteresis typical of the semiconductor-to-metal transition in VO<sub>2</sub> was seen in measurements of the variation of electrical resistance with temperature for film H.

The processes by which films I and J were produced were both successful. In 30 producing film I, the substrate temperature was 465°C; in producing film J, the substrate temperature was 490°C. A hysteresis typical of the semiconductor-to-metal transition in VO<sub>2</sub> was seen in measurements of the variation of electrical resistance with temperature for film I and film J.

In the production of film K, zinc was introduced as a dopant. Consequently, film K was a zinc-doped VO<sub>2</sub> film. The film exhibited a good change in resistance with temperature associated with the semiconductor-to-metal transition. The width of the observed hysteresis loop was relatively narrow.

5

#### Example of a preferred process

The experimental data were analysed, in order to derive a preferred method and set of process conditions for reliably producing good VO<sub>2</sub> films by spray pyrolysis in accordance with the invention.

10

A precursor solution is prepared by dissolving approximately 0.228M vanadyl acetylacetonate ([VO(acac)<sub>2</sub>]) in a 2:1 by volume mixture of ethanol to 7% by volume acetic acid in water. Preferably, the precursor solution may be prepared not more than 48 hours prior to use.

15

The precursor solution is then deposited on to a substrate by spray pyrolysis in a humid atmosphere.

In this preferred example process, the carrier gas is pure nitrogen, which is supplied to the nozzle of the spray pyrolysis system at a flow rate of 14.5 l/minute. Alternatively, the carrier gas may be water-saturated nitrogen. At the same time, the precursor solution is introduced into the nozzle at a flow rate of 1 ml/min. Droplets of the precursor solution are thereby produced at the nozzle, and carried to the substrate and deposited thereon.

20  
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A glass substrate is used, which is held at a temperature of 490°C during spray deposition. The duration of the spray deposition process is approximately 40 minutes.

Following the spray deposition process, the deposited material and the substrate are held at 490°C for a further 30 minutes. The deposited material forms a film on the substrate. Typically, the film has a thickness of approximately 300 nm.

30

The person skilled in the art will appreciate that the process conditions used to produce the films A-K and of the preferred process may be varied without departing from the scope of the invention.

- 5 In another example embodiment of the invention, vanadium (IV) oxide was deposited as a film by spray pyrolysis using vanadium (V) oxide ( $V_2O_5$ ) as a precursor.

0.236 g  $V_2O_5$  and 0.6 g oxalic acid solid precursors were dissolved in 25 ml of water and warmed until a blue vanadyl oxalate ([VO(ox)]) solution was formed. 15 ml of  
10 the [VO(ox)] solution was sprayed, with nitrogen as a carrier gas, at a rate of 0.5 ml/min on to a glass substrate held at  $500^\circ\text{C}$ . The deposited film was then annealed at  $525^\circ\text{C}$  under flowing nitrogen for three hours. Optionally, acetone may be added to the [VO(ox)] solution.

- 15 The  $VO_2$  film produced was uneven and powdery. Figure 6 is an XRD spectrum of the  $VO_2$  film. Peaks corresponding to the (011), (211), (020), (212) and (021) planes are labelled in Figure 6.

In another example embodiment of the invention, vanadium (IV) oxide was deposited  
20 as a film by spray pyrolysis using vanadium (V) oxide ( $V_2O_5$ ) as a precursor.

0.103 g  $V_2O_5$  and 0.2 g oxalic acid solid precursors were dissolved in 10 ml of water and warmed until a blue [VO(ox)] solution was formed. The [VO(ox)] solution was  
25 sprayed, with nitrogen as a carrier gas, at a rate of 1.0 ml/min on to a glass substrate held at  $450^\circ\text{C}$ . The deposited film was then annealed at  $525^\circ\text{C}$  under flowing nitrogen for three hours. Optionally, acetone may be added to the [VO(ox)] solution.

The  $VO_2$  film produced was relatively uniform and thin. Figure 7 is an XRD spectrum  
30 of the  $VO_2$  film. Peaks corresponding to the (100) and (011) are labelled in Figure 7.

Methods using an oxalate precursor, e.g. oxalic acid, may be preferred, since oxalate precursor materials generally may be relatively cheap. In addition, the films formed by methods using an oxalate precursor may be relatively clean.

There are two vanadyl oxalates,  $[\text{VO}(\text{ox})(\text{H}_2\text{O})_2]$  and  $[\text{VO}(\text{ox})_2]^{2-}$ . When the vanadium (IV) oxalate is produced by dissolving  $\text{V}_2\text{O}_5$  in an excess of an oxalate solution, more of the dianionic complex ( $[\text{VO}(\text{ox})_2]^{2-}$ ) than the neutral complex ( $[\text{VO}(\text{ox})(\text{H}_2\text{O})_2]$ ) typically may be present.

5

In embodiments of the invention, dopants may be added to the solution, in order to modify the film produced. Suitable dopant precursor materials may include water-soluble metal salts, e.g. a water-soluble tungsten salt.

10 The production process of the present invention has several advantages over known methods of producing vanadium (IV) oxide films.

Importantly, in some embodiments, the metal, e.g. vanadium, generally may not change oxidation state during the spray pyrolysis process, i.e. the metal exists in the same oxidation state in the precursor complex as in the final film. Without wishing to  
15 be bound by any theory, it is thought that this results in the metal oxide film, e.g. vanadium (IV) oxide film, produced in accordance with the invention being of very good purity (i.e. at least 90% pure).

20 The coordination and decomposition chemistry of precursor vanadyl complexes means that the spray pyrolytic process of the invention is successful. The complexes decompose, i.e. the ligands become separated from the vanadyl ions, due to the temperature of the substrate. The water provides the oxygen that is required to react with the vanadyl ion to produce vanadium (IV) oxide ( $\text{VO}_2$ ). Preferably, the water  
25 may be the principal, e.g. only, source of oxygen available for the reaction. The water may be provided by an aqueous solution (e.g. an aqueous precursor solution) and/or an aqueous solvent mixture and/or a water-containing (e.g. water-saturated) carrier gas.

While knowledge of coordination and decomposition chemistry of targeted precursors  
30 (e.g. the coordination and decomposition chemistry of targeted vanadyl precursors such as  $[\text{VO}(\text{acac})_2]$  and  $[\text{VO}(\text{ox})]$ ) underpins this invention, in further developing the invention the spray pyrolytic process has been tested, controlled, developed and optimised.

For example, the process allows for the production of metal oxide films, e.g. vanadium (IV) oxide films, at lower temperatures than flame spray pyrolysis. Also, the process may be more acceptable from an environmental and/or health and safety perspective than processes such as APCVD. One environmental benefit is that the process may provide the ability to produce metal oxide films, e.g. vanadium (IV) oxide films, from an aqueous precursor solution.

Furthermore, careful selection of the precursor complex can reduce or minimise any harmful emissions (e.g. nitrous oxide) when the precursor complex decomposes. For example, the acetylacetonate (acac) ligand has reasonable water solubility and does not produce very harmful emissions on decomposition of the precursor complex, making it a suitable choice for use in the present invention. The oxalate (ox) ligand has good water solubility and also does not produce very harmful emissions on decomposition of the precursor complex, making it a suitable choice for use in the present invention.

Advantageously, the process can be scaled up to produce relatively large, very pure doped or undoped films.

As a result of the use of aqueous solutions, relatively low temperatures and/or low-harmful emission ligands, the equipment cost and complexity for practising the invention may be relatively low. Thus, it may be relatively economical to scale-up the invention. Furthermore, since the ligand(s) may remain intact after decomposition of the precursor complex, in some embodiments, it may be possible to recover the ligand(s) and subsequently re-use the recovered ligand(s) in the preparation of the precursor complex. Thus, the ligand(s) may be recyclable, thereby further reducing or minimising the cost of practising the invention.

Advantageously, the process may form part of a float glass manufacturing process for smart windows. The process may be carried out in-line with the float glass process. Accordingly, the process may enable the efficient production of smart windows.

While the invention has been described specifically in relation to the production of vanadium (IV) oxide films, it will be appreciated that other metal (IV) oxide films may be produced by the process of the invention. For instance, the spray pyrolytic process of the invention may be used to produce doped or undoped molybdenum (IV)

oxide films, tungsten (IV) oxide films, germanium (IV) oxide films or manganese (IV) oxide films.

In addition, the process may be utilised to produce metal oxide films, in which the  
5 metal has other oxidation states. For instance, the process may be utilised to produce  
metal (II) oxide films or metal (III) oxide films such as vanadium (III) oxide films.

It will be appreciated that the methods of the invention are typically performed in an  
inert atmosphere and generate intermediate oxidation states. By performing the  
methods in an inert atmosphere, advantageously the formation of higher, e.g. highest,  
10 oxidation states is avoided.

**Claims**

1. A process for producing a metal oxide film comprising:  
providing a precursor solution or dispersion containing a metal complex;  
5 spraying the precursor solution on to a heated substrate in the presence of  
water, thereby depositing material on the substrate; and  
drying the deposited material, thereby producing the metal oxide film.
2. A process according to claim 1, wherein the precursor solution is an aqueous  
10 solution.
3. A process according to claim 1 or claim 2, wherein the concentration of the  
precursor solution is up to 0.1M.
- 15 4. A process according to claim 1, claim 2 or claim 3, wherein the metal oxide  
film comprises, or consists essentially of, a metal (IV) oxide film ( $\text{MO}_2$ , where M is a  
metal) or the metal oxide film comprises, or consists essentially of, a metal (III) oxide  
film ( $\text{M}_2\text{O}_3$ , where M is a metal).
- 20 5. A process according to any one of the preceding claims, wherein the metal is  
vanadium, molybdenum, tungsten, germanium or manganese.
6. A process according to claim 5, wherein the metal is vanadium and the metal  
complex is vanadyl acetylacetonate, or wherein the metal is vanadium and the metal  
25 complex is vanadyl oxalate.
7. A process according to claim 5, wherein the metal is molybdenum and the  
metal complex is molybdenyl acetylacetonate, or wherein the metal is molybdenum and  
the metal complex is molybdenyl oxalate or a suitable molybdenum (IV) complex.  
30
8. A process according to any one of the preceding claims, wherein the oxidation  
state of the metal is the same in the metal complex as it is in the metal oxide film.
9. A process according to any one of the preceding claims, wherein the precursor  
35 solution comprises one or more further metals as dopants.

10. A process according to claim 9, wherein the precursor solution containing the dopant(s) is supplied to a nozzle and sprayed on to the heated substrate; and/or wherein the dopant(s) is/are supplied to a nozzle separately from the precursor solution or dispersion containing the metal complex and the dopant(s) is/are mixed  
5 with the precursor solution or dispersion containing the metal complex at the nozzle immediately before spraying; and/or one or more solutions or dispersions containing the dopant(s) is/are sprayed from one or more different nozzles from the precursor solution or dispersion containing the metal complex, such that the solutions or dispersions mix together as they are sprayed on to the substrate.
- 10
11. A process according to any one of the preceding claims, wherein the precursor solution or dispersion is sprayed on to the heated substrate in a controlled and/or a protective and/or an inert atmosphere.
- 15
12. A process according to any one of the preceding claims, wherein the precursor solution or dispersion is sprayed on to the heated substrate with the aid of a carrier gas.
13. A process according to any one of the preceding claims, wherein the precursor  
20 solution is sprayed on to the heated substrate at a rate of up to 5 ml/min.
14. A process according to claim 12, or claim 13 when dependent on claim 12, wherein the carrier gas is sprayed at a rate of up to 60 ml/min.
- 25
15. A process according to any one of the preceding claims, wherein the substrate is heated to a temperature of at least 150°C, at least 175°C, at least 300°C, at least 400°C, at least 450°C and/or up to 550°C.
16. A process according to any one of the preceding claims, wherein drying the  
30 deposited material comprises maintaining the substrate at a predetermined drying temperature for a predetermined drying time.
17. A process according to claim 16, wherein the predetermined drying temperature is at least 150°C, at least 175°C, at least 300°C, at least 400°C, at least  
35 450°C and/or up to 550°C.



18. A process according to claim 16 or claim 17, wherein the predetermined drying time is at least 5 minutes and/or up to 60 minutes.
19. A process according to any one of the preceding claims comprising heat  
5 treating, e.g. annealing, the deposited material.
20. A process according to claim 19, wherein the heat treating is carried out in an inert atmosphere.
- 10 21. A process according to any one of the preceding claims, wherein the steps of spraying the precursor solution on to a heated substrate in the presence of water, thereby depositing material on the substrate and drying the deposited material are repeated one or more times.
- 15 22. A process according to any one of the preceding claims, wherein the process comprises the step of, after drying (for the last time), cooling the deposited material on the substrate.
- 20 23. A process according to any one of the preceding claims, wherein the pH of the precursor solution is at least 5 and/or up to 9.
24. A process according to any one of the preceding claims, wherein the method comprises a step of preparing the precursor solution.
- 25 25. A process according to any one of the preceding claims, wherein the substrate comprises glass.
26. A process according to claim 25, wherein the substrate comprises a ribbon of float glass floating on a bath of molten metal.
- 30 27. A process according to any one of the preceding claims, wherein the substrate is stationary or moving.

28. A product comprising a substrate with a film thereon, the film comprising or consisting essentially of a metal oxide film obtained or obtainable by the process of any one of claims 1 to 27.

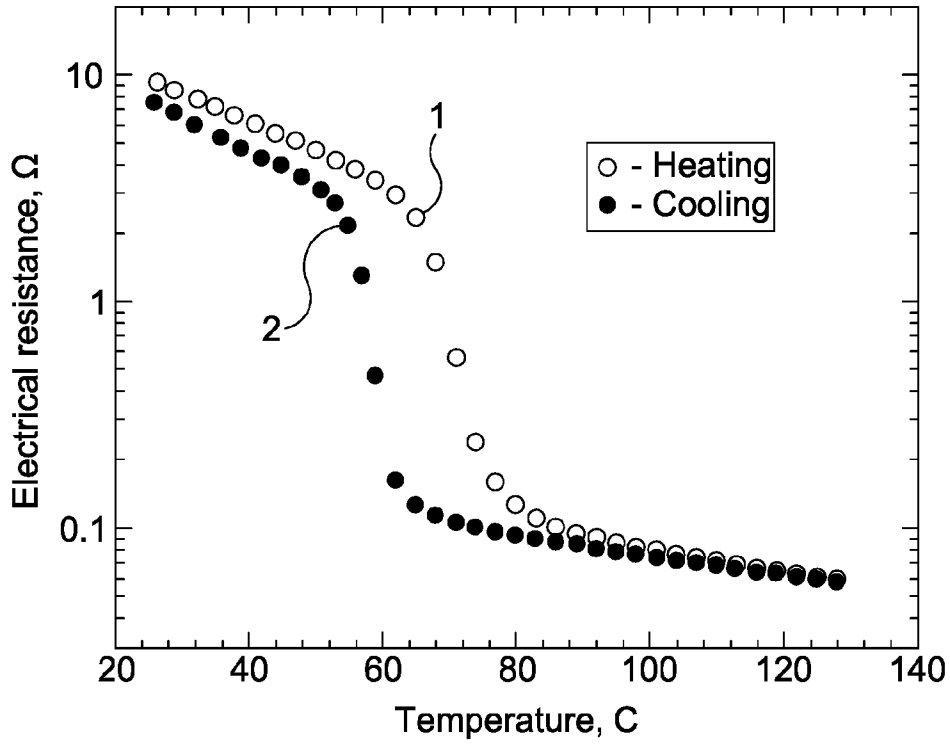


Figure 1

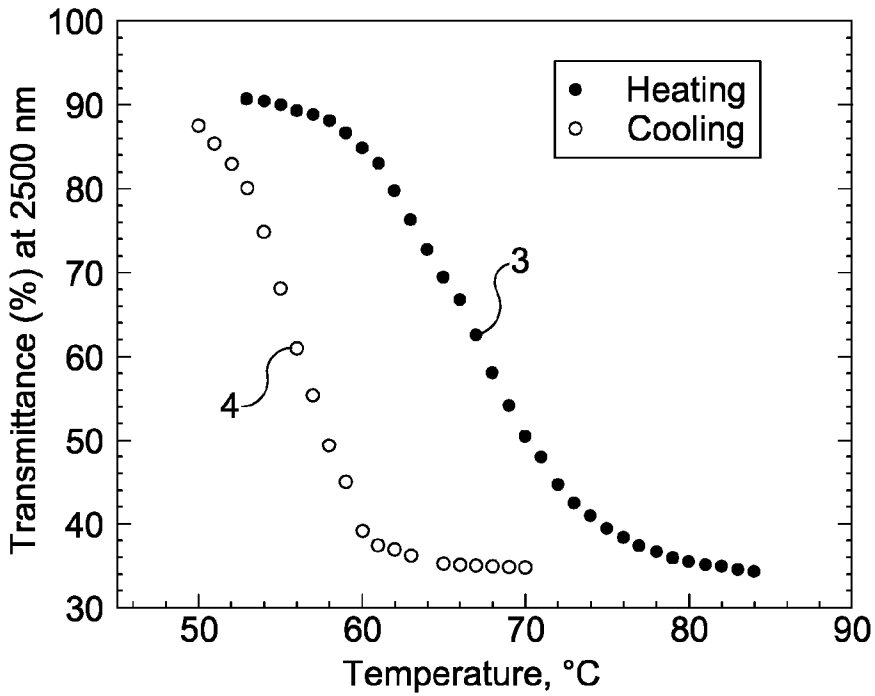


Figure 2

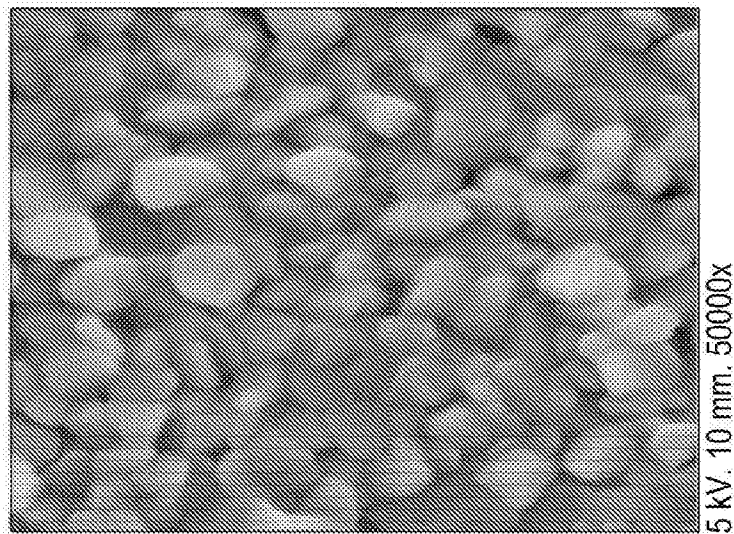


Figure 3

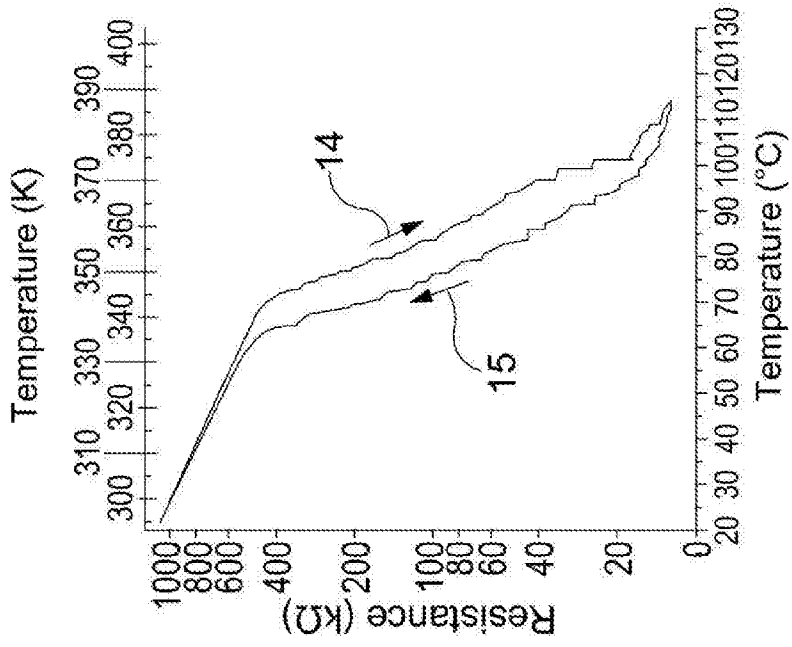


Figure 4

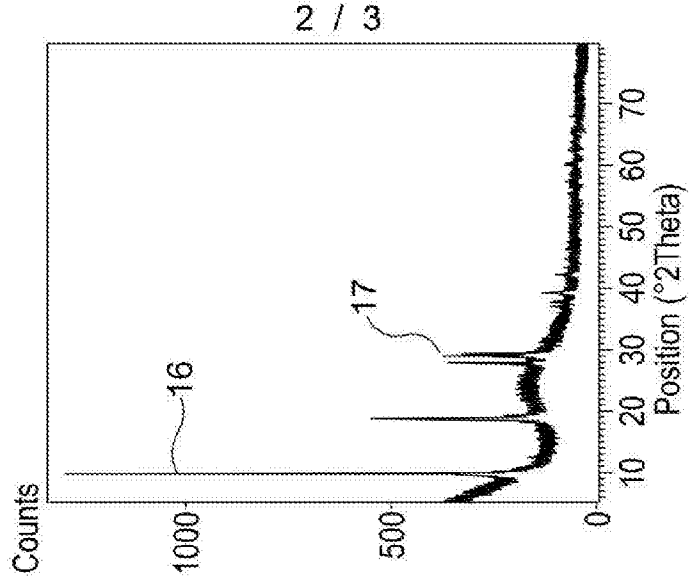


Figure 5

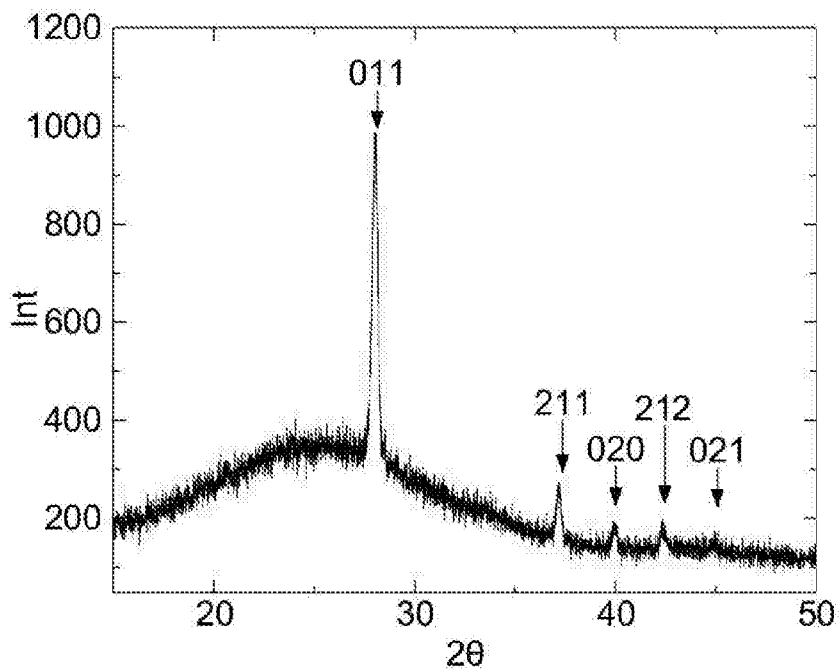


Figure 6

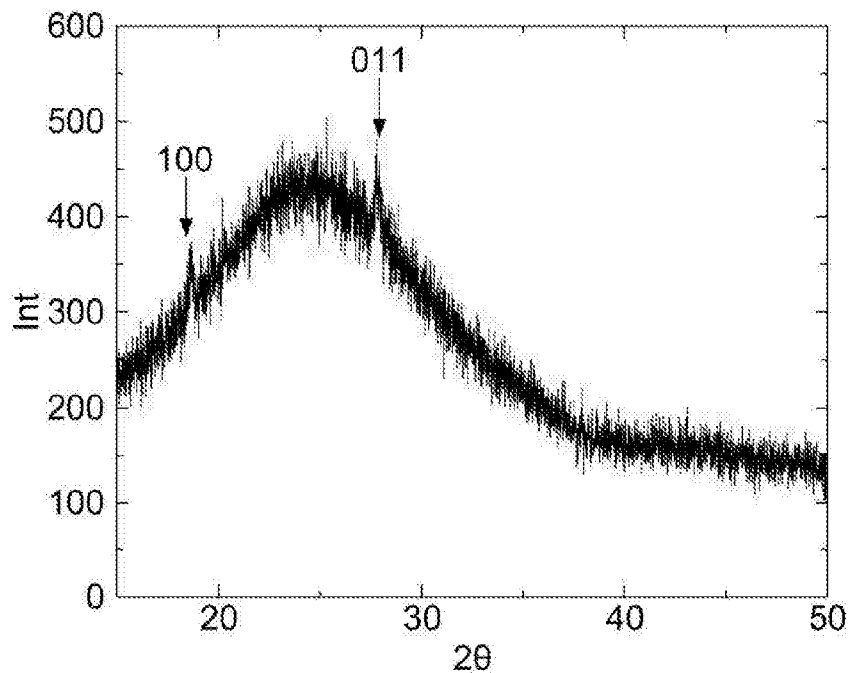


Figure 7

**INTERNATIONAL SEARCH REPORT**

International application No  
PCT/GB2017/050296

**A. CLASSIFICATION OF SUBJECT MATTER**  
 INV. C03C17/10 C23C18/12 C03C17/25  
 ADD.  
 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)  
 C03C C23C

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 practicable, search terms used)  
 EPO-Internal, 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	US 4 129 434 A (PLUMAT EMILE ET AL) 12 December 1978 (1978-12-12) example 2	1-6,8, 10-28
X	US 3 850 665 A (POSSET R ET AL) 26 November 1974 (1974-11-26)  example 2	1,2,4-6, 8-10, 12-19, 21-28
X	US 4 855 161 A (MOSER FRANK H [US] ET AL) 8 August 1989 (1989-08-08)  example 10	1,2,4-8, 10,11, 13-22,28

Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents :

<p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier application or patent but published on or after the international filing date</p> <p>"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)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p>	<p>"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</p> <p>"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</p> <p>"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</p> <p>"&amp;" document member of the same patent family</p>
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Date of the actual completion of the international search  12 April 2017	Date of mailing of the international search report  24/04/2017
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Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016	Authorized officer  Saldamli, Saltuk
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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/GB2017/050296

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		JP S63303076 A 09-12-1988	
		US 4855161 A 08-08-1989	
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