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(54) Producing a layer of transparent conductive zinc oxide.

(57) A process for providing a layer (15) of an optionally doped transparent electrically conductive zinc oxide on a heated substrate (8) in which a solution of a thermally decomposable precursor for the zinc oxide is sprayed towards the substrate and the spray is subjected to sufficient radiant heating firstly to evaporate the solvent and create a particulate residue and secondly to cause the residue to sublime. The residue is adsorbed onto the substrate or growing layer and undergoes surface diffusion and pyrolysis leading to growth of the layer of zinc oxide. The layer is probably nucleated and has a high degree of ordering between adjacent crystallites. Also a layer of zinc oxide having planes in its crystalline structure which are predominantly orientated parallel with the surface of the substrate.

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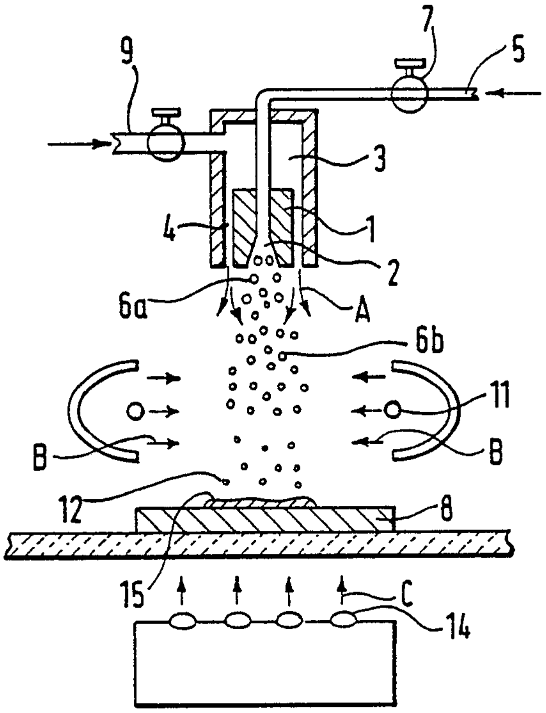

FIG.1.

PRODUCING A LAYER OF TRANSPARENT CONDUCTIVE ZINC OXIDE

This invention relates to a process for producing a layer of transparent electrically conductive zinc oxide on a substrate in which process a precursor for the zinc oxide is thermally decomposed. The invention also relates to an improved layer of transparent electrically conductive zinc oxide which can be produced by the process. Such layers are alternatively called "thin films".

Electrically conductive zinc oxide is a non-stoichiometric oxide of zinc in which the atomic ratio of zinc to oxygen is other than 1:1, usually being 1:0.7 to 0.97. The conductivity of the oxide may be improved by adding dopants such as indium, aluminium or terbium in amounts of from for example 0.05 to 0.6at% (atomic %). Layers of non stoichiometric zinc oxide find uses in the reflection of heat, the protection of materials from ultraviolet light, the detection of oxidising or reducing gases and the dissipation of static electricity, in luminescent devices, display devices, transparent heating elements, transducers, thermionic convertors and as optical wave guides and active or passive elements in photovoltaic or photo-electrochemical cells. Most of these uses require the layer of zinc oxide to extend over a large area and to be free from major variations in optical, electrical and/or structural properties.

Layers of non-stoichiometric zinc oxide on substrates have been produced by processes such as chemical vapour deposition, vacuum deposition or sputtering but engineering limitations make such processes unsuitable for the deposition of zinc oxide over large areas of substrate. The processes are also slow and expensive to perform. An alternative process in which a precursor for zinc oxide is pyrolysed was described by Major et al in "Thin Solid Films" volume 108 pages 333 to 340, 1983. Major et al spray an alcoholic aqueous solution of zinc acetate and indium chloride onto a hot glass substrate where heat conducted from the substrate causes the alcoholic aqueous solvent to evaporate leaving a residue which pyrolyses to produce a layer of non stoichiometric zinc oxide doped with indium. Attempts to produce large areas of zinc oxide result in layers which show unacceptably wide variations in optical, electrical and structural properties so that the process has only been used to produce small areas (less than 70mm by 25mm) of zinc oxide. Even then, the layers produced show major variations in thickness. For example a layer intended to have a thickness of 0.2µm can show variations of ± 0.1µm. The process is also slow to perform taking as long as 45 minutes or more to produce a layer of 0.2µm nominal thickness.

An object of this invention is to provide an improved process for producing a layer of transparent electrically conductive zinc oxide on a substrate and especially a process suitable for use over larger areas of substrate. Another object is to provide an improved zinc oxide. Objects of refinements of the invention include the provision of a process which is quicker to perform and the provision of layers of transparent conductive zinc oxide which have less variation in thickness and/or improved optical, electrical or structural properties.

Accordingly this invention provides a process for providing a layer of transparent electrically conductive zinc oxide on a substrate in which a solution (in a preferably polar solvent) of a thermally decomposable precursor for the zinc oxide is converted to droplets, the droplets are heated to evaporate the solvent and the substrate is heated to a temperature high enough to decompose the precursor wherein the process also comprises

a) subjecting the droplets to radiant heating to evaporate the solvent without the solvent coming into contact with the substrate or the zinc oxide layer and to leave a particulate residue and

b) causing the residue to contact the heated substrate or layer of zinc oxide being produced on the substrate.

It is probable that zincic material from the residue sublimes and adsorbs onto the surface of the substrate or the layer of zinc oxide and undergoes surface diffusion and pyrolysis leading to the nucleation of a growing layer of zinc oxide.

Such use of radiant heating to evaporate the solvent before it reaches the substrate or layer of zinc oxide has been found to permit the achievement of a much more uniform temperature in the substrate, in the residue and in the layer of zinc oxide as it grows on the substrate. This in turn allows the layer to be produced over much larger areas of substrates, for example areas of over 100mm by 100mm.

Temperature uniformity at the surface of the substrate or zinc oxide layer and in sublimed material close to the substrate is further enhanced by using radiant heating to heat the substrate thereby ensuring a rapid and steady transfer of heat. This is important in promoting a highly uniform pyrolysis of the precursor and growth of the layer. In particular it promotes nucleation of the crystalline structure of the growing layer. The temperature of the substrate is preferably from 350 to 450°C.

The preferred method for converting the solution into droplets is to expel the solution under pressure through an aperture. Generally a solution pressure of from 15 to 35 bar is suitable and a convenient aperture comprises an elliptical orifice having a major diameter of from 50 to 200µm. Preferably the orifice is located about 200 to 400mm above the substrate.

It is also preferred to use a stream of non-oxidising (preferably inert) carrier gas to assist in conveying the droplets from the aperture towards the substrate. This is conveniently arranged by causing the carrier gas under a positive pressure (preferably 0.5 to 2 bar above atmospheric) to issue from a gas outlet or series of outlets located around the aperture so that the droplets are exposed to a curtain of carrier gas as soon as they emerge from the aperture. The stream of carrier gas merges with the stream of droplets causing a reduction in their size and a reduction in the number of collisions between droplets. The use of the carrier gas therefore creates a finer and more uniform stream of droplets which in turn leads to a finer residue and a more uniform growth of the layer. The stream of carrier gas can also be used to control the speed of the droplet stream. The preferred carrier gas is nitrogen.

The stream of droplets may be heated by passing the stream between a pair of optical heating elements. The elements may be a pair of commercially available tungsten halogen heating tubes of 500 to 1500 watts positioned horizontally each at about 40 to 140mm either side of the stream.

Preferred precursors have a melting point of from 120 to 350°C (especially 220 to 300°C) and of course they must be soluble in a (preferably polar) solvent. The concentration of the precursor is preferably 0.05 to 0.2 molar. The preferred precursor is zinc acetate but zinc chloride may be used. A pyrolisable soluble salt of a dopant may be added to the solution, for example indium chloride, aluminium nitrate or terbium chloride. Generally indium is the preferred dopant.

The polar solvent preferably has a boiling point of from 60 to 115°C at 1 bar and may be for example water or an alcohol such as methanol or isopropanol. Mixtures of water and alcohol are preferred because they have been found to control the oxidation of the residue and thereby improve conductivity. The mixture is preferably made by mixing one volume of water with from 2 to 4 volumes of alcohol. It is preferred to acidify an alcoholic solvent slightly to achieve for example a pH of about 4 to 6.

It is preferred to impart a trochoidal motion to the substrate in order to optimise the uniformity of thickness of the layer of zinc oxide. Generally the substrate is subjected to a reciprocating movement of amplitude 50 to 150mm on which is superimposed an eccentric rotational motion having a radius of eccentricity of from 15 to 50mm.

An important feature of the process of this invention is the large number of variables which can be adjusted to control the process. Variables which can be adjusted are the flow rate of the solution to the aperture, the intensity of the heating applied to the droplets or to the substrate and also material close to the substrate, the distance between the substrate and the aperture from which the droplets emerge, the pressure of the solution and hence the rate at which droplets emerge from the aperture, the pressure of the carrier gas and hence the speed of the stream of droplets, the concentration of the precursor in the solvent and the composition of the solvent and hence its volatility. These factors are easily adjusted to ensure that solvent evaporates in transit from the aperture towards the substrate and before it contacts the substrate or zinc oxide layer. They can also be adjusted to optimise the growth rate of the layer. Usually a layer of 2.0µm thick can be grown in less than 20 minutes with a variation in thickness over an area of 100mm by 100mm of less than 0.05µm.

The electrical properties of the layers (especially undoped layers) may be improved further by annealing under a non-oxidising atmosphere. For example annealing may be carried out by heating the layer to a temperature of from 390 to 500°C (preferably 390 to 430°C) for a period of up to 20 minutes. Annealing is preferably performed for at least 5 minutes but little advantage has been gained by annealing for more than 15 minutes. Annealing does not significantly affect the structural properties or optical properties in the visible wavelengths but transmission of infra red wavelengths was reduced.

The process of this invention can be used to produce a layer of non stoichiometric zinc oxide having a crystalline structure which grows in a direction preferred for the achievement of improved optical and electrical properties and which probably arises because of nucleation of the growing layer by material diffusing in the layer. Accordingly this invention provides supported on the surface of a substrate a layer of transparent electrically conductive zinc oxide having a crystallite structure in which the ratio of zinc to oxygen atoms is from 1:0.8 to 1:0.97, in which the zinc oxide has a characteristically hexagonal structure and in which the crystallites are ordered such that their (0002) planes lie predominantly parallel to the surface of the substrate which is to say that their "c" axes are perpendicular to that surface. It has been found that the presence of dopant in the zinc oxide does not significantly affect the hexagonal structure but changes the preferred orientation such that the (1120) planes of the crystallites lie predominantly parallel to the surface of the substrate which is to say their "c" axes are inclined at 20°C from the normal to the substrate. A predominant orientation of the (0002) or (1120) planes can be detected using reflection high energy electron diffraction (RHEED). The predominantly orientated structure produces a diffraction pattern consisting of a plurality of concentric semicircles each defined by several discontinuous arcs whereas the unorientated structure produces similarly concentric semicirles but each is defined by one continuous arc. RHEED may be performed according to the method described by G J Russell in "Progress in Crystal Growth and Characterisation", volume 5, 1985 pages 291 to 391, the contents of which are herein incorporated by reference. Layers up to 1.6 µm in thickness usually have optical transmissions for visible light (wavelenth 450 to 630nm) of over 85% and transmissions of up to 90% are often achievable in thicknesses of 0.39 to 1µm with reflection factors for the same spectral range of only 2 to 5%.

Layers 1.0µm thick and doped with 2 at % indium were obtained with resistivities of 5 x 10^{-3} ohm.cm or better and sheet resistances of under 300 ohm/square. These could be further improved by annealing to values as low as 1 x 10^{-3} ohm.cm and 30 ohm/square using optimised conditions. Annealed undoped layers tend to have resistivities of 10^{-1} to 10^{-2} ohm.cm and sheet resistances of from 200 to 300 ohm/square at thicknesses of 1.0µm.

The invention is further illustrated by the following preferred embodiment described with reference to the drawings in which

Figure 1 is a diagrammatic representation of apparatus suitable for performing a process according to this invention and Figure 2 is an underneath plan view of the nozzle arrangement in the apparatus.

Figure 1 shows a nozzle 1 comprising a conical orifice 2 whose sides are inclined 35° to the vertical. Orifice 2 is elliptical in cross-section as shown in Figure 2 and the major internal diameter of the ellipse at the base of nozzle is 80µm. Nozzle 1 is located within a chamber 3 which defines an annular outlet 4 surrounding orifice 2. The clearance between nozzle 1 and chamber 3 is 3mm.

A solution of precursor for zinc oxide is conveyed under pressure into nozzle 1 by pipe 5 whereupon the pressure gradient across orifice 2 converts the solution into droplets 6a and expels them towards glass substrate 8 located 300mm below nozzle 1. The flow rate of solution along pipe 5 can be adjusted by means of a valve 7. Non-oxidising gas is pumped under positive pressure through pipe 9 into chamber 3 whence it issues (as indicated by arrows A) via outlet 4 forming a curtain around the droplets 6a. Gas from the curtain merges with the stream of droplets 6a and reduces their size to form smaller droplets 6b. Droplets 6b pass through beams of radiant heat indicated by arrows B which heats them directly and very rapidly. The beams are emitted by opposed commercial 750 watt tungsten-halogen heating tubes 11, each 150mm long and positioned horizontally 150mm from the centre of the stream of droplets. The process variables (especially the solution flow rate) are adjusted to ensure that the solvent content of the droplets evaporates before reaching substrate 8 leaving a shower of fine particles of residue 12 to fall towards substrate 8 thereby avoiding any localised chilling caused by solvent evaporating from a solid surface.

Substrate 8 is supported on a transparent ceramics domestic cooker hob 13 which is subjected to trochoidal motion in a horizontal plane to improve the uniformity of the deposition. The troichoidal motion consists of a reciprocating motion having an amplitude of 100mm on which is superimposed an eccentric rotational motion having a radius of eccentricity of 30mm. Substrate 8 and hob 13 are heated directly and rapidly by radiant heat (indicated by arrows C) from an array of four 450 watt domestic tungsten halogen heating lamps 14. A layer of transparent electrically conductive zinc oxide 15 grows on glass substrate 7 and as it grows, it too is heated directly and rapidly by lamp 14.

The invention is further illustrated by Examples 1 and 2.

EXAMPLE 1

A precursor solution was made by forming a 0.1M solution of zinc acetate in a mixture of alcohol and water made by mixing 3 volumes of isopropyl alcohol with 7 volume of water. The pH of the solution was adjusted to 5 by adding acetic acid.

A glass substrate was placed on the ceramics hob of the apparatus shown in Figure 1 and then both substrate and hob were heated to 390°C. During performance of the process the temperature of the substrate was monitored and maintained at a steady 390°C. When the substrate had reached a steady temperature, nitrogen gas under a pressure of 1.5 bar was pumped into the chamber followed by delivery of the precursor solution to the nozzle under a steady pressure of 21 bar. The solution was then converted to droplets by its passage through the orifice and the flow rate of the solution was adjusted using the valve so as to ensure that the solvent in the droplets evaporated before reaching the substrate so as to create a particulate residue and also to ensure that the residue sublimed just before reaching the substrate. The flow rate was adjusted within the range 25 to 30ml/min. A nucleated layer 100mm by 100mm and 0.39µm thick of transparent electrically conductive zinc oxide was grown on the substrate to which it was found to adhere well.

The layer was next annealed by heating it to a temperature of 400° C for 15 minutes in an atmosphere of equal partial pressures of hydrogen and nitrogen. On cooling, the layer was found to have a hexagonal crystalline structure with (0002) planes predominantly orientated parallel to the surface of the substrate. The layer had an optical transmission to visible light of 90%, a reflectance of up to 6%, a resistivity of 10^{-2} ohm.cm, a sheet resistance of 300 ohm/square, a free electron carrier concentration of $10^{19}/cm^3$ and an electron mobility value of $30cm^2/V$ sec.

EXAMPLE 2

The procedure of Example 1 was repeated except that the precursor solution also contained enough indium chloride to produce a zinc oxide containing 2 at.% of indium as a dopant.

A layer was obtained which had a thickness of 1.6µm and had the hexagonal structure but with (1120) planes predominantly parallel to the surface of the substrate. Again the optical transmission was 90% with a reflectance of about 8%. Before annealing the resistivity of the layer was 10^2 ohm.cm, the sheet resistance was 100ohm/square, the free electron carrier concentration was $10^{20}/cm$ and the mobility was from 1 to 2 cm^2/V sec. After annealing, resistivity fell to 5×10^{-4} ohm.cm, sheet resistance to 30 ohm/square whilst mobility rose to over $10cm^2/V$sec. Carrier concentration did not change significantly.

Layers produced according to Examples 1 and 2 could be applied to areas of 100mm by 100mm with variations in thickness of less than ±0.05µm and to areas of 150mm by 150mm with variations of less than ± 0.1µm. They adhered well to glass and had abrasion resistance comparable with that of other transparent conductive oxide layers.

Claims

1. A process for providing a layer (15) of transparent electrically conductive zinc oxide on a substrate (8) in which a solution of a thermally decomposable precursor for the zinc oxide is converted to droplets (6a 6b), the droplets (6b) are heated to evaporate the solvent and the substrate is heated to a temperature high enough to decompose the precursor wherein the process also comprises

a) subjecting the droplets to radiant heating (10) to evaporate the solvent without the solvent coming into contact with the substrate or the zinc oxide layer and to leave a particulate residue (12) and

b) causing the residue to contact the heated substrate or layer of zinc oxide being produced on the substrate.

2. A process according to Claim 1 wherein the heating is sufficient to cause the residue to sublime before it reaches the surface of the substrate or layer of zinc oxide.

3. A process according to Claim 1 wherein the substrate is heated by means of radiant heating (14).

4. A process according to Claim 3 wherein the substrate is heated to 350 to 450° C.

5. A process according to any one of the preceding Claims wherein the solution is converted to droplets by expulsion under pressure through an aperture (2).

6. A process according to Claim 5 wherein a stream of a non oxidising carrier gas is caused to issue from at least one outlet (4) located around the aperture and is allowed to merge with the droplets expelled from the aperture.

7. A process according to any one of the preceding Claims in which the layer of zinc oxide produced is subjected to an annealing process by heating the layer to 390 to 500° C for at least 5 minutes under a non-oxidising atmosphere.

8. A process according to Claim 7 wherein the non-oxidising atmosphere comprises a mixture of hydrogen and nitrogen.

9. Supported on the surface of a substrate (8), a layer (15) of transparent electrically conductive zinc oxide having a crystallite structure in which the ratio of zinc to oxygen atoms is from 1:08 to 1:0.97 and in which the zinc oxide has a characteristically hexagonal crystalline structure and in which the crystallites are ordered such that their (0002) planes lie predominantly parallel to the surface of the substrate.

10. Supported on the surface of a substrate (8) a layer (15) of transparent electrically conductive doped zinc oxide having a crystallite structure in which the ratio of zinc to oxygen atoms is from 1:08 to 1:0.97, in which the dopant comprises 0.05 to 0.6 at % of indium, aluminium or terbium, in which the zinc oxide has a characteristically hexagonal crystalline structure and in which the crystallites are ordered such that their (1120) lie predominantly parallel to the surface of the substrate.

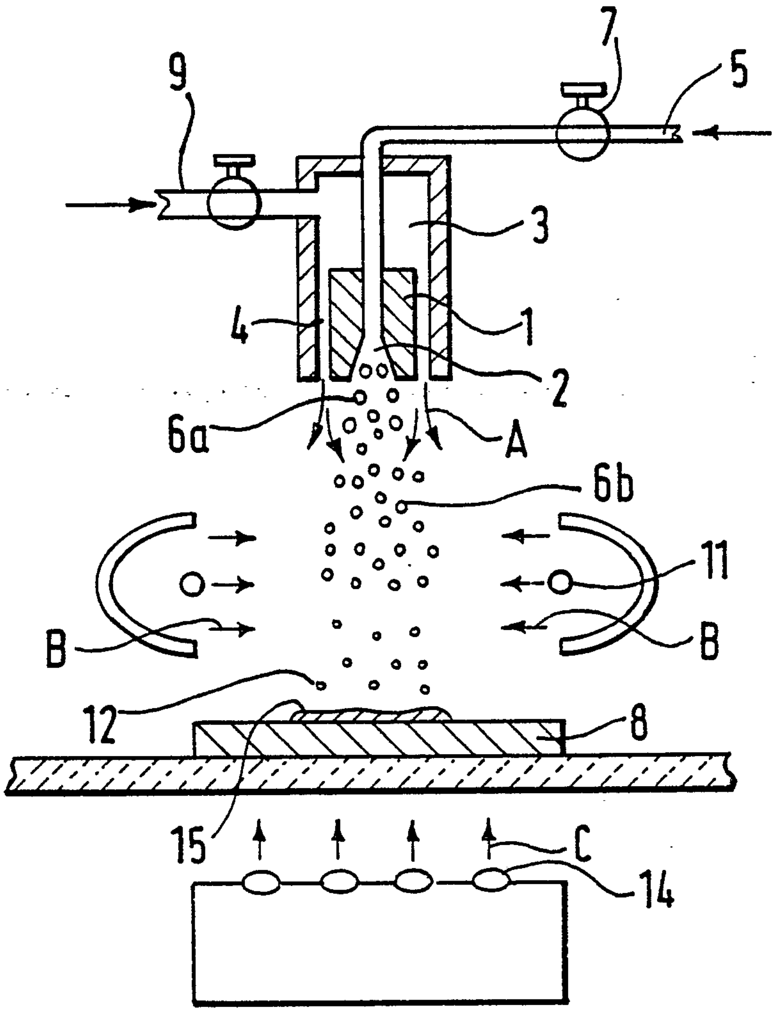

FIG. 1.

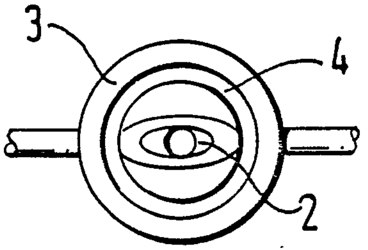

FIG. 2.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number

EP 89 30 2495

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.4)
A	US-A-2 791 521 (JAFFE) ---		C 23 C 18/12
A	GB-A- 704 793 (PITTSBURGH PLATE GLASS CO.) -----		
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 23 C C 03 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	23-06-1989	NGUYEN THE NGHIEP

CATEGORY OF CITED DOCUMENTS

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