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(54) Title: INDIUM TIN OXIDE

(57) Abstract: A method of preparing indium tin oxide (ITO) and such an oxide per se are described. The method involves calcining a precursor material that includes a source of indium, a source of tin and an oxygen scavenging means. The oxygen scavenging means may be an organic polymer such as an acrylamide. The precursor material may be prepared in a cryogenic or precipitation process. Use of the process may produce a relatively low resistivity ITO.

INDIUM TIN OXIDE

This invention relates to mixed metal oxides and particularly, although not exclusively, relates to the preparation of indium tin oxide (ITO) and such an oxide *per se*.

Transparent conducting oxides (TCO's), of which ITO is one of the most important, are essentially transparent to visible light but possess useful electroconductivity. In general, TCO's, and, in particular, ITO can be used to form transparent and/or conductive films, coatings, paints, and adhesives having one or more of a number or properties, including antistatic, anti rusting/corrosion, electric field/electromagnetic wave shielding, UV shielding, anti reflection, low reflective, anti streaking, improved scratch resistance, hardness, chemical resistance, and weather resistance. Among the applications in which the indium tin oxide is useful are printing electrode patterns, display devices, LC displays, touch screens, electroluminescent (EL) lamps, EMI shielding window, cathode ray tubes, architectural windows, flexible and rigid membrane switch displays, solar batteries, PDP (personal display devices), and glass security sensors.

The technology of choice for deposition of ITO (or indeed any TCO) in a manufacturing environment is d.c. magnetron sputtering using a metal or ceramic target coupled with careful control of the atmosphere. Large quantities of ITO are utilised commercially to coat polyester sheet in a vacuum roll process. This is often used as the top conducting electrode in EL-lamp displays. These typically have a sheet resistance of 50-500 Ω/□ and transparency of 80-90%. There are however alternative methods of depositing the clear conductive layer that offer much greater scope in the choice of substrate. This technology is based upon functional inks utilising for example screen printing to build a device in layers onto practically any substrate. There is therefore a requirement for a TCO which can be incorporated as a pigment into a binder/solvent system, which can then be printed onto a substrate and dried down to give a film with the desired electrical and optical properties.

The requirements for a TCO are a large band gap >3 eV and a conduction band shape that ensures the plasma edge lies in the infrared. Typically the host structure will allow the introduction of a large number of degenerate carriers by a combination of non-stoichiometry and alieo-valent doping. Although a great many TCO's (both p-type and n-type) are known, ITO (an n-type) is believed to have the best combination of properties and is relatively easy to synthesise.

Various processes are known for preparation of ITO that generally involve hydrolysis or precipitation of water-soluble precursors by acid or base. For example, US5529720 describes the preparation and calcination of In/Sn co-precipitate hydroxides. US 5071800 describes a process which involves thermal decomposition of indium/tin mixed acetate. US 6051166 describes the calcination of precipitates containing indium and tin.

It is an object of the present invention to provide a process for producing ITO which may be improved over known processes.

According to a first aspect of the invention, there is provided a method of preparing ITO which includes the step of calcining a precursor material which includes a source of indium, a source of tin and an oxygen scavenging means.

It has been found, in accordance with embodiments of the present invention, that ITO produced using a precursor material as described has a low resistivity compared to ITO produced in an identical manner except in the absence of a said oxygen scavenging means. Without being limited by this statement, it is believed that the oxygen scavenging means can scavenge oxygen during calcination to restrict the filling of oxygen vacancies in the ITO crystal structure and thereby facilitate preparation of ITO of reduced resistivity.

Said oxygen scavenging means is preferably a chemical means, for example a chemical compound which is able to react with products, for example decomposition products produced or present in the method, especially with such products produced during calcination of the precursor material. Such products may be produced by decomposition of compounds included in said precursor material. Said scavenging means, or a decomposition product thereof which may be produced during calcination, may form covalent bonds with products or intermediates produced by decomposition of compounds included in said precursor material.

When compounds included in said precursor material include a sulphate compound, said scavenging means is preferably arranged to scavenge a product of sulphate decomposition that may occur. If the calcination process is carried out in air, then said scavenging means may also react with oxygen in air.

Said scavenging means may be arranged to form SO_2 from decomposition products produced during calcination.

Said scavenging means may be arranged to produce CO_2 from decomposition products produced during calcination.

Said scavenging means may be arranged to produce H_2O from decomposition products produced during calcination.

Said scavenging means is suitably arranged to decompose during calcination. Thus, its decomposition temperature is preferably less than the temperature at which calcination is carried out.

The amount of scavenging means in said formulation may be 0.9 to 2 times the amount required to fully reduce the products of the decomposition of the source of indium (e.g. indium sulphate) to indium oxide. The amount may be 1.1 to 1.8 times, preferably 1.3 to 1.7 times, more preferably 1.4 to 1.6 times, especially about 1.5 times the amount required as aforesaid.

The amount of scavenging means may be 0.9 to 2 times the mole equivalents of the source of indium (e.g. indium sulphate) in said formulation. The amount may be 1.1 to 1.8 times, preferably 1.3 to 1.7 times, more preferably 1.4 to 1.6 times, especially about 1.5 times the amount described as aforesaid.

Said scavenging means is preferably an organic material. Said scavenging means is suitably a polymeric material and is preferably an organic polymeric material. Said polymeric material preferably includes a repeat unit which consists of atoms selected only from carbon, hydrogen, oxygen and nitrogen atoms. Said repeat unit preferably consists of the aforementioned atoms.

Said polymeric material preferably has a molecular weight in the range 5000 to 100000 amu, more preferably in the range 5000 to 50000 amu.

Said polymeric material preferably has a Tg of at least 25°C, preferably at least 75°C, more preferably at least 125°C. The Tg may be less than 400°C, preferably less than 200°C.

Said polymeric material is preferably water soluble. Preferably, at least a 20wt%, more preferably at least a 40wt%, especially at least a 50wt% solution of said polymeric material in water at 25°C can be prepared.

Said polymeric material is preferably completely water miscible at 25°C.

Said polymeric material is preferably wholly soluble in 0.25 molar indium sulphate solution at 25°C.

Said polymeric material may include a $-NH_2$ moiety in its repeat unit. Said polymeric material preferably includes an amide moiety in its repeat unit. Said polymeric material is preferably an acrylamide.

Said scavenging means is preferably intimately mixed with the sources of indium and tin in said precursor material.

Whilst said oxygen scavenging means could be incorporated into said precursor material just prior to calcining, it is preferably introduced upstream thereof. It is preferably introduced when said precursor material has a different physical or chemical state or composition compared to its state or composition at the time it is calcined. For example, when said precursor material is prepared by hydrolysis or precipitation it may be added prior to such hydrolysis or precipitation. When said precursor material is prepared in a cryogenic process, is preferably added prior to a low temperature treatment step in the preparation of said precursor material.

Said precursor material may be prepared in a process which involves hydrolysis, precipitation or cryogenic processing of compounds arranged to produce said precursor material.

When a process involves hydrolysis or precipitation, the process may involve selecting water soluble precursor salts, preferably incorporating said scavenging means there into, and causing hydrolysis or precipitation of the salts, preferably by addition of acid or base. The hydrolysis product or precipitate (suitably incorporating said scavenging means) may then be isolated thereby to define a said precursor material that is calcined in the method. A preferred precursor material prepared as aforesaid is a hydroxide, for example indium hydroxide.

When a process involves cryogenic processing, as is preferred, the process may include the step of:

1) causing a liquid formulation which includes a solvent to form a solid, wherein the formulation includes:

    (i) an indium compound, a tin compound and ammonium sulphate; or

(ii) $(NH_4)In(SO_4)_2$ and a tin compound.

The liquid formulation of step (a) is preferably an aqueous formulation. Thus said formulation preferably includes a major amount of water as solvent.

In the context of the present specification, a "major amount" means that at least 70wt%, suitably at least 80wt%, preferably at least 90wt%, especially at least 99wt% of a specified material is present.

The solvent of step (a) preferably consists essentially of water.

The liquid formulation of step (a) is preferably at a temperature of greater than 0°C, more preferably greater than 5°C, especially at ambient temperature prior to it being caused to form a said solid.

Step (a) preferably includes causing the liquid formulation to cool, suitably to a temperature that is at or below the freezing point of the liquid formulation. Suitably, the liquid formulation is introduced into a low temperature environment which is at a temperature of less than -25°C, preferably less than -50°C, more preferably less than -100°C, especially less than -150°C. Said environment may be at ambient pressure. Said environment may comprise a low boiling liquid at the temperature stated. Said low boiling liquid is preferably inert and/or unreactive towards any part of the formulation. Said liquid preferably comprise a material that is gaseous at STP. Said liquid preferably comprise liquid nitrogen, for example boiling liquid nitrogen.

In step (a), said liquid formulation is preferably caused to form particles of solid. Suitably, less than 10wt%, preferably less than 5 wt%, more preferably less than 1 wt%, especially substantially no particles formed in step (a) and treated in step (b) described hereinafter have a particle size of less than 100μm. Preferably, a major amount of said particles are in the range 100μm to 2mm. Alternatively, it is possible to produce particles in step (a) having a mean size of around 100μm although such particle-size distributions are less preferred as the smaller particle sizes present may result in loss of material/handling difficulties in the subsequent steps.

Said particles are preferably caused to form in step (a) by spraying said liquid formulation into said low temperature environment. Said low temperature environment, for example said low boiling liquid, may be contained within a receptacle closed at one end or may define a column wherein the liquid formulation is atomised into a counter-current of said low boiling liquid. The particles may then be

isolated by an appropriate technique. For example, when said low temperature environment is provided by a low boiling liquid, the particles may be separated by liquid being decanted or the particles may be filtered to achieve separation.

The ratio of the number of moles of indium ions in said indium compound to the number of moles of tin ions in said tin compound in said liquid formulation is suitably in the range 5 to 50, preferably 10 to 40, more preferably 15 to 30, especially 18 to 23.

The ratio of the number of moles of ammonium ions in said ammonium compound (e.g. ammonium sulphate or ammonium indium sulphate) to the number of moles of tin ions in said tin compound in said formulation is suitably in the range 5 to 50, preferably 10 to 40, more preferably 15 to 30, especially 18 to 23.

Preferably, the liquid formulation comprises the materials of (a)(i). In this case, the ratio of the number of moles of indium ions in said indium compound to the number of moles of ammonium ions in said ammonium sulphate is suitably in the range 0.6 to 1.5, preferably 0.8 to 1.3, especially 0.9 to 1.1. Also, in this case, the ratio of the number of moles of tin ions in said tin compound to the number of moles of ammonium ions in said ammonium sulphate is suitably in the range 0.01 to 0.1, preferably 0.02 to 0.08, especially 0.03 to 0.07.

Said liquid formulation of step (a)(i) may include at least 0.4 wt% of said tin compound (and preferably less than 5wt%, more preferably less than 3wt%), at least 2wt% of ammonium sulphate (and preferably less than 10wt%, more preferably less than 7wt%), at least 10wt% of said indium compound (and preferably less than 30wt%, more preferably less than 25wt%, especially less than 20wt%), and at least 60wt% of solvent (especially water) (and preferably less than 80wt%, more preferably less than 70wt%).

Said liquid formulation of step (a)(ii) may include at least 0.4 wt% of said tin compound (and preferably less than 5wt%, more preferably less than 3wt%), at least 12wt% of $(NH_4)In(SO_4)_2$ (and preferably less than 35wt%, more preferably less than 30wt%, especially less than 25wt%) and at least 60wt% of solvent (especially water) (and preferably less than 80wt%, more preferably less than 70wt%).

Said tin compound used in steps (a)(i) or (a)(ii) is preferably a Sn(II) compound. It may be tin (II) sulphate or tin (II) fluoride. Preferably, it is tin (II) sulphate.

If said liquid formulation includes more than one type of indium compound or more than one type of tin compound, the above-mentioned amounts/ratios preferably refer to the sum of the amounts of indium and tin ions in such compounds as appropriate. Preferably, however, said liquid formulation includes only a single type of indium compound and a single type of tin compound.

Preferably, the indium compound and ammonium sulphate of step (a)(i) are adapted to produce $(NH_4)In(SO_4)_2$. Thus, the compounds of (a)(i) may upon contact and/or reaction therebetween produce the compounds of (a)(ii).

Said liquid formulation of step (a) of the method preferably includes said scavenging means.

Said scavenging means is preferably dissolved in said liquid formulation selected for treatment in step (a) of the method. Each of the compounds of step (a)(i) and (ii) selected for treatment in step (a) are preferably in solution in said liquid formulation.

Said liquid formulation of step (a)(i) or (ii) may include at least 1wt%, preferably at least 2wt% (and preferably less than 5wt%, more preferably less than 4wt%) of said scavenging means.

Said liquid formulation used in step (a) is preferably substantially homogenous.

The solid prepared in step (a) suitably includes the compounds of (a)(i) or (ii), preferably $(NH_4)In(SO_4)_2$, scavenging means and frozen solvent, especially water, included initially in said liquid formulation of step (a).

Cryogenic processing preferably includes a step (b) which comprises conditioning a solid comprising the compounds described in step (a)(i) or (a)(ii). The solid is preferably prepared as described in step (a)(ii).

In said conditioning step (b), a part of the solid is preferably caused to undergo a change, for example a physical change. Preferably, in step (b), the crystallinity of the solid is changed. Preferably, conditioning is arranged to increase the crystallinity of at least a component of said solid. Preferably, conditioning is arranged to increase the crystallinity of the solvent, especially water. Initially, the solvent, in admixture with the other components, may be in a relatively amorphous state. Conditioning is preferably arranged to increase its crystallinity. Preferably, said solvent is substantially crystalline after said conditioning. Said conditioning may comprise devitrification of said solid.

Step (b) may include raising the temperature of the solid (suitably by at least 5°C, preferably by at least 10°C). Preferably, the difference between the lowest temperature to which the solid is subjected in step (a) compared to the highest temperature to which it is subjected in step (b) is at least 50°C, more preferably at least 100°C. Preferably, conditioning includes raising the temperature of the solid prepared in step (a); and maintaining the solid at a raised temperature for at least 5 minutes, preferably at least 15 minutes, more preferably at least 25 minutes. Step (b) may include raising the temperature in steps. It may be raised to a first raised temperature and held at the temperature; and subsequently raised to a second temperature and held at the temperature. Preferably in step (b), the maximum temperature attained by the solid is less than 0°C, more preferably less than -10°C, especially less than -20°C.

Step (b) preferably comprises annealing the solid.

The process preferably includes a step (c) which comprises selecting a solid which incorporates solvent and includes the compounds described in (a)(i) or (a)(ii) and causing removal of solvent from said solid. The solid is preferably prepared in accordance with steps (a) and/or (b) above.

Step (c) preferably includes causing vaporisation, preferably sublimation of the solvent. The step preferably includes applying energy, for example heat, to provide the latent heat of vaporisation of the solvent.

Step (c) is preferably carried out at less than ambient pressure. It may be carried out at a pressure of less than 100 Pa, preferably at less than 50 Pa, more preferably at less than 20 Pa, suitably in a vacuum. Step (c) may be carried out at 10-20 Pa.

Step (c) is suitably carried out at a shelf temperature of greater than 5°C, preferably greater than 15°C, more preferably greater than 20°C. Step (c) is preferably carried out wholly at a shelf temperature of less than 80°C, more preferably less than 60°C.

Step (c) may involve raising the temperature of the solid, for example prepared in step (b), suitably gradually and in a vacuum; holding the solid at the raised temperature, suitably for at least one hour; raising the temperature further and holding the solid at the raised temperature, suitably for at least 1 hour, preferably at least 10 hours.

Preferably, after step (c), the solid includes less than 1 wt%, more preferably substantially no, solvent, for example water

The step of calcining a said precursor material in accordance with the invention of the first aspect may involve calcining following any or all of steps (a), (b) and/or (c) as described.

The step of calcining said precursor material in accordance with the invention of the first aspect preferably includes subjecting said precursor material to an environment wherein the temperature is at least 400°C, preferably at least 600°C, more preferably at least 800°C. The temperature may be less than 1200°C, preferably less than 1000°C. Suitably, the solid is subjected to a temperature in the range 400°C to 1200°C (more preferably 800°C to 1000°C) for at least 10, preferably at least 20 minutes. It is preferably held at a temperature within said ranges for less than 1 hour.

Preferably, the solid is calcined in an inert gas atmosphere, for example in a nitrogen atmosphere.

The ITO produced in the method preferably has a powder resistivity in the range 0.1 to 0.5 Ω.cm, more preferably in the range 0.2 to 0.5 Ω.cm measured at less than 30% volume fraction, more preferably when measured at less than 25% volume fraction. The BET surface area may be less than $35m^2/g$, suitably less than $30m^2/g$, preferably less than $25m^2/g$, more preferably less than $20m^2/g$, especially $17m^2/g$ or less. The BET surface area may be at least $10m^2/g$.

The invention extends to a paint, ink or resin comprising ITO as described.

A particular application for ITO as produced by the method of the present invention or as defined in any preceding aspect is in various optical display devices, including electroluminescent (EL) lamps. EL lamps are thin, electrically stable multilayer devices that generally consist of front and rear electrodes and phosphor and dielectric layers located between the electrode layers. The front electrode is an actual conductive substrate that is screen or rotary screen-printed and may comprise the ITO on a polyester film. In early EL lamps the plates consisted of glass and ceramic, but have evolved into the thin plastic films that are commonly utilized today. The multi-layer structure of the EL lamp requires that the phosphor be excited with an alternating current to generate the field effect to energize the phosphor so causing it to emit light. In order to allow the light generated by the phosphor to escape, the

front electrode containing the ITO must be at least semi-transparent. EL lamps are utilized in a wide variety of applications, including watches, pagers, membrane keyboards, sports shoes, safety vests, point of sale signs, vehicles, aircraft and military equipment.

Accordingly, the invention also extends to an electroluminescent lamp comprising ITO made by the method according to the invention.

Any feature of any aspect of any invention or embodiment described herein may be combined with any feature of any aspect of any other invention or embodiment described herein mutatis mutandis.

Specific embodiments of the invention will now be described, by way of example, with reference to the accompanying drawings, in which:

Figure 1 is a schematic summary of steps in the preparation of indium tin oxide (ITO);

Figure 2 is an outline of key steps in cryogenic processing of a formulation adapted to produce ITO;

Figure 3 is a schematic representation of a solid-solid transformation of indium sulphate;

Figures 4a to 4c show the structure of In_2O_3, InO_3 doped with tin and an ITO structure with oxygen vacancies filled;

Figure 5 illustrates the effect of added polymer on powder resistivity for three levels of polymer additions;

Figure 6 is a schematic representation of apparatus for measuring conductivity.

Figure 7 is a schematic representation of a crucible; and

Figure 8 is a block diagram an in-line double jet precipitation apparatus.

Various methods are available for synthesizing indium tin oxide powder (ITO) that may be used, for example, in screen printable inks. One method involves precipitating an indium and tin compound from aqueous solutions of indium and tin-containing salts. For example, the indium and tin compound may be synthesized from indium nitrate and tin chloride in water by addition of ammonia. Alternatively, an indium and tin compound may be prepared from indium chloride, tin chloride and

sodium hydroxide. The precipitates prepared may be calcined at high temperature to produce ITO.

Another method is summarised in Figure 1. It involves (A) preparing a homogenous aqueous solution of precursor salts, for example $In_2(SO_4)_3$, ammonium sulphate and $SnSO_4$; (B) spraying the solution into liquid nitrogen or a cold gas whereupon the droplets formed are rapidly frozen; (C) conditioning the frozen droplets by annealing them; followed by (D) freeze drying to remove frozen ice by sublimation leaving behind a molecular mixture of the precursor salts as a dry powder. This mixture is then (E) calcined to effect a transformation to ITO.

The doping of an indium oxide lattice with a higher valence metal than In3+ (i.e. Sn4+) introduces electrons into the system by virtue of the charge neutrality as illustrated below using the Kroger and Vink notation:

$$SnO_2 + In_{In}^{x} \rightarrow Sn_{In}^{\bullet} + In_2O_3 + e^{'}$$

As the valence band is filled, the electrons go into the conduction band (cb). Consequently, the ITO is an intrinsic n-type semi-conductor and more doping should lead to higher electrical conductivity.

Figure 4(a) illustrates the structures of In_2O_3, which is the C2 rare earth type structure; Figure 4(b) shows substitution of two In^{3+} ions for Sn^{4+} ions.

Due to the existence of oxygen vacancies as illustrated in Figure 4, it is not inevitable that more doping will increase conductivity since in the calcination step (E) (Figure 1) molecular oxygen produced can fill the vacancies, as illustrated in the equation below (and in Figure 4c wherein one of the oxygen vacancies has been filled with O^{2-}), stripping electrons from the conduction band in the process

$$O_2(g) + 4e^{'} + 2V_o^{x} \rightarrow 2O_o^{''}$$

As a consequence, it is possible to prepare indium oxide which is highly doped with tin but which, nonetheless, has relatively poor (compared to other materials prepared as described herein) electrical properties.

As illustrated hereinafter, it has been determined that it is possible to reduce the powder resistivity of ITO produced after calcination by incorporating into a mixture which is calcined an oxygen scavenging material which is arranged to react with

oxygen that may be present and/or produced during calcination and effectively restrict the filling of oxygen vacancies by oxygen.

A preferred oxygen scavenging material is one that can be sacrificially consumed during calcination. The scavenging material may be incorporated into an ITO precursor formulation at any stage in the process. For example, when the ITO precursor formulation is prepared by hydrolysis or precipitation of water-soluble precursors by acid or base, the scavenging material may be incorporated after precipitation of the precursors; or it may be included in a solution that includes the precursors. When the ITO precursor formulation is prepared in a cryogenic process, as described in Figure 1, the scavenging material is preferably incorporated with precursor salts, prior to cryogenic treatment.

Preferred scavenging materials are water-soluble polymers. Preferred polymers for use as scavengers have a relatively high Tg (which may in particular make the formulation for use in step (A) of Figure 1 more handleable) and are water soluble and compatible with the low pH and ionic strength that may be encountered in the preparation of the ITO precursor formulation. Polyacrylic acid (PAA) and polyacrylamide (PAM) can be used.

A particularly preferred polymer is a 50wt% polyacrylamide aqueous solution comprising polyacrylamide of molecular weight about 10,000 amu and a Tg of 140°C. This can be added directly to a solution comprising ITO precursors (for example the formulation for use in step (A) of figure 1) in the desired amount and requires minimal dissolution time.

One preferred method of preparing low resistivity ITO that may be used in screen printable inks is the aforementioned cryogenic process, summarised in Figure 1. Referring to Figure 1, precursor salts selected for step (A) of the process must have high solubility in water; be capable of being freeze dried in step (D) at conventional shelf temperatures (0-50°C) and pressures (100-500 mbar); and be capable of being calcined in step (E) to yield ITO without melting which would destroy the structure generated during freezing (step (B)) and annealing (step (C)) processes. It has been found that indium salts such as $InCl_3$, $In(NO_3)_3$ and $In_2(SO_4)_3$ alone collapse if they are freeze dried at temperatures above around –30°C (due to liquification of amorphous water in the structure) which makes their use potentially time-consuming and expensive. However, it has been found that the addition of ammonium sulphate to the aqueous formulation in step (A) results in formation of a solution of

$(NH_4)In(SO_4)_2$ which can be freeze dried at a desired temperature in a reasonable time scale. Thus, in the formulation of step (A), the indium compound is provided by inclusion of ammonium sulphate together with an indium salt, in particular indium sulphonate $(NH_4)In(SO_4)_2$. The scavenging material, especially PAA or PAM is also included with the salts and it is found that this remains intimately mixed with the salts during the various process steps.

Similarly, tin in higher valence states, such as $SnCl_4$, is prone to collapse during freeze drying and, additionally, the use of halides is undesirable because of potential for corrosion of the furnace during step (E). It has been found that the tin dopant can be successfully introduced using $SnSO_4$ as a precursor. A less preferred alternative is tin (II) fluoride (SnF_2).

In a preferred embodiment, the formulation used in step (A) comprises $In_2(SO_4)_3$ and ammonium sulphate (which produce $In(NH_4)(SO_4)_2$) together with $SnSO_4$.

In step (B), the formulation prepared in step (A) is sprayed by atomisation into liquid nitrogen whereupon drops are rapidly frozen to yield small intimately mixed particles of the precursor salts with ice crystals. The cryogenic processing described essentially uses phase transformations to generate fine microstructure. The key steps in the process are illustrated in Figure 2. Very high super-cooling is used as the driver for phase separation. A major feature therefore, is that creation of the particle is not governed by chemistry or mixing but by temperature and cooling rate that may be more reproducible and easier to control. Ultimately complete freezing leads to the formation of a new solid phase that is an intimate mixture (usually on a molecular level) of the starting precursors. This in turn is mixed with ice crystals on a microscopic level leading to the formation of fine microstructure. This mixing at different levels ultimately leads to the formation of ITO that is different to ITO made by other known means.

As described above, some salts may collapse when freeze dried in step (D) and this is undesirable, since particles prepared may then be difficult to re-disperse. The origin of the collapse is that during freezing in step (B) all or part of the ice fails to crystallise but forms a vitreous glass. As a consequence, during freeze drying there comes a point when the frozen structure liquefies and falls apart, leading to collapse of the structure formed by the precursor salts.

To obviate the risk of collapse, step (C) is undertaken, wherein the frozen particles prepared in step (B) are subjected to low temperature annealing by conditioning the frozen powder at temperatures between –30 to –20°C for 30 minutes to 2 hours. The higher the temperature of annealing, the shorter the annealing time required. It has been shown, by Isothermal DSC, that this treatment causes glassy parts of the frozen particles to crystallise, wherein water is transformed to ice and possibly, although not necessarily, there may be recrystallisation of the solute. This transition is called devitrification which occurs at a temperature in the range -35°C to -20°C and is accompanied by a release of heat. Devitrification results in removal of water from the vitreous glass with the net result that the Tg of the frozen particles is raised, making sublimation of the ice in step (D) possible without collapse.

An alternative, but much less preferred embodiment, involves storing the frozen particles of step (B) at low temperature for a long time. However, whilst crystallisation of water is thermodynamically favoured, it is kinetically very slow at low temperatures.

In step (D), the frozen crystalline water is removed without disruption of the newly created morphology. This is achieved by sublimation of the solvent phase in a process called lyopholisation or, from an engineering perspective, freeze-drying. By converting the solvent phase directly to vapour without a liquid intermediate ensures minimal disruption of the solid phase i.e. capillary pressures and secondary growth are avoided. The net result is almost perfect preservation of the solid phase morphology.

Freeze-drying may be undertaken at a temperature in the range 0 to 50°C and a pressure in the range 100-500 mbar. In general terms, freeze-drying is undertaken under conditions such that the material treated does not melt (which may be a possibility if the freeze drying temperature is too high).

In step (E), the freeze dried $In(NH_4)(SO_4)_2/SnSO_4$ material is subjected to a thermal treatment which comprises calcination in a furnace at a temperature in the range 800 to 1000°C at ambient pressure. The thermal decomposition of the $In(NH_4)(SO_4)_2$ has been shown by DSC to take place in three steps. The first starts below 100°C and is completed by 200°C and comprises removal of bound water. Next, at 300°C, the thermal decomposition of ammonium sulphate begins which appears to be a three-step process; the process is completed by 600°C. At 700°C the decomposition of indium sulphate begins and is complete by 800°C. The decomposition is believed to

result in the production of the cubic phase of indium oxide, together with sulphur trioxide, sulphur dioxide and oxygen. As shown in Figure 3, the solid–solid transformation described is believed to proceed via a gaseous interface.

In the case of tin(II)sulphate, at 350°C, DSC reveals a phase transition which is believed to be a change in its crystal structure. Thermal decomposition occurs sharply at 490°C which is believed to be in accordance with the following equation:

$$SnSO_4(s) \longrightarrow SnO_2(s) + SO_2(g)$$

Thus, calcination temperatures of greater than 800°C are required for complete decomposition. Calcination of the material can be achieved without melting.

After calcination, it has been observed that there are no XRD lines or pattern due to SnO2 and that the normal XRD pattern for indium oxide has been slightly displaced indicating some lattice substitution of tin for indium. The colour of the mixed oxide is pale green compared to the canary yellow of indium oxide when not doped by tin. Thus, this confirms the synthesis of indium tin oxide.

In the calcinations step, it is believed that that oxygen scavenging material reacts with excess oxygen from the sulphate decomposition according to the following equation

$$SO_3 \rightarrow SO_2 + \tfrac{1}{2}O_2$$

It is believed that the oxygen scavenger (represented below as a hypothetical carbon chain polymer) combines in the calcination step with SO_3 or O_2 to produce SO_2, CO_2 and H_2O, according to the equations:

$$(-CH_2-) + 3SO_3 \rightarrow 3SO_2 + CO_2 + H_2O$$

$$2(-CH_2-) + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

If sufficient polymer is added this should eliminate the problem and preserve the oxygen vacancies.

The polymer was formulated to the indium sulphate in accordance with the following equation:

$$5In_2(SO_4)_3 + 2(-CH_2CHCONH_2) \rightarrow 5In_2O_3 + 15SO_2 + 6CO_2 + 5H_2O + N_2$$

Thus, a ratio of 518g (1 mole) of indium sulphate to 28.4g (0.4 moles of the repeat unit) of polyacrylamide is just sufficient to oxygen balance the system. Note that the ammonium sulphate is not referenced in the above equation since it decomposes before the indium sulphate and so is not relevant. Tin sulphate is not referenced since it decomposes without producing O_2 or SO_3.

In order to gauge the effect of polymer addition on ITO prepared, samples were prepared with 5% mole equivalents tin and polymer in the range of 50-150% mole equivalents of oxygen balance. These were studied by Differential Thermal Analysis/Thermogravimetric Analysis.

It was found that with polymer present at 150% of the oxygen balance, the decomposition of the ammonium sulphate was largely unaffected; however, the indium sulphate decomposition was complete at little over 600°C. Thus, the polymer had in effect lowered the calcination temperature by about 200°C.

It has been found that addition of polymer as described fundamentally changes the nature of the decomposition. Samples were calcined at 900°C as before and compared to those processed without polymer. The effect is quite dramatic (as illustrated in Figure 5) with an almost ten-fold increase in the performance of the powder in the resistivity test of Figure 6 described hereinafter. The powder resistivity is found to compare favourably with commercially available ITO but, advantageously, this can be achieved at lower powder volume fractions.

The level of polymer addition affects properties of the ITO. It is possible with a large excess of polymer to sinter the ITO giving highly conductive, low surface area dense particles. Similarly, it is possible to use less polymer and retain the fluffy, high surface area obtained without polymer addition.

The following analytical methods may be used to analyse materials prepared as described herein.

Analytical Method 1 – measurement of resistivity/conductivity and density.

The powder electrical conductivity was measured by compacting a small sample if material and measuring the resistance of it. The arrangement for measuring the conductivity is shown in Figure 6 and this provides a convenient and rapid means of assessing the viability of a particular powder.

The sample 50 to be tested is first weighed and inserted between two pistons 52, 54 held in place with a glass sleeve 56. A micrometer 55 is used to measure the position of a ram 60. The voltage and current are measured and displayed as a resistance (R) whilst an incrementally increasing force is applied to the sample, up to a maximum force of 5.4 MPa. The simple cylindrical geometry allows the powder resistivity (r) to be measured by the relationship

$$r = \frac{RA}{d}$$

where A is the cross-sectional area of the sample holder and d is the measured distance. The powder volume fraction is calculated from the following

$$\phi = \frac{dA}{\rho_o}$$

where ρ_o is the density of crystalline indium oxide (taken as 7.1 gcm^{-3}). In a typical test the resistivity as a function of powder volume fraction is plotted. This gives information not only on the electrical properties but also how compactable

Analytical Method 2 – Measurement of BET surface area

The BET surface area was measured by first outgassing the sample over nitrogen at 100°C and then measuring the nitrogen sorption at liquid nitrogen temperature using a Micromeritics APSP2400.

Specific examples of the preparation of ITO are provided below.

In each of the following examples, which involve calcinations in air, a frusto-conical cruicible as shown in Figure 7 was used for containing samples. This has diameters "a" and "b" of 40mm and 78mm respectively; and a height "c" of 65mm.

The bed depth of material calcined in the crucibles was 20mm – 30mm in the processes of Examples 1 to 6.

Unless otherwise stated all materials were used as received from Aldrich UK. The indium salt described was obtained from the Indium Corporation of the USA.

Example 1 (Comparative)

Anhydrous indium(III) sulfate (58.5g, 0.111 mol) was slowly added with agitation to demineralised water (240g, 13.3 mol) at ambient temperature. Ammonium sulphate (14.7g, 0.111 mol) and tin(II) sulphate (2.5g, 0.012 mol) were subsequently added. Stirring was continued until a clear slightly yellow solution was obtained.

The solution was sprayed into boiling liquid nitrogen using a drop generator, which consists of a metal plate that allows predrilled holes of variable size to be inserted. In the present example an arrangement with 5 x 0.5 mm holes was used. At the end of the process the excess liquid was carefully decanted and frozen particles recovered. A narrow frozen particle size distribution with no particles below 100 μm was produced.

The frozen droplets were placed onto trays that were pre-cooled in a batch freeze dryer at –40°C. The frozen powder was spread evenly onto each tray to a bed depth of 10-15 mm.

Annealing and freeze drying were carried out in a conventional batch freeze dryer which utilises a 24 hour cycle using a fixed programme. The product was first warmed to -40°C and held there for 30 minutes. The shelf temperature was then raised to -25°C and held there for 1 hour to anneal the product. The temperature was then lowered to –40°C and held for a further 10 minutes. This completed the annealing process.

A vacuum was then applied 0.13 mBar (100 mTorr) and the shelf temperature raised to 25°C over a period of 2 hours. It was then held at this temperature for a further 4 hours. The temperature was then raised to 40°C over a period of 2 hours and then held there until the end of the drying period (a total time of 20-24 hours). The product leaving the dryer was completely free of ice.

The dried ITO precursor was then calcined by placing material in crucibles which were then quickly placed into a muffle furnace set at 900°C in ambient air. The product was removed from the furnace after 1 hour and quenched by discharging the hot powder directly onto a metal tray at room temperature. It was observed that the initially white precursor was green after calcination and the volume of material was reduced by a factor of about three-quarters.

The resistivity at maximum load, measured in accordance with Analytical Method 1 above was 5.3 Ω.cm and the powder volume fraction was 21.1%.

Example 2

The following formulation was prepared by the method described in Example 1 and analysed as described in Analytical Methods 1 and 2. The resistivity and powder volume were 0.42 Ω.cm and 19% respectively.

Indium(III) Sulphate	57.5g, 0.111 mol
Ammonium Sulphate	14.75g, 0.111 mol
Tin(II) Sulphate	2.5g, 0.012 mol
Water	240g, 13.3 mol
Polyacrylamide Solution*	9.6g, 1.5 mole equiv.

*The polycarylamide solution comprised a 50%wt solution in water of a polymer of molecular weight 10,000 amu. 1 mole equivalent is 64g of this solution.

The effect the addition of polymer has on the resistivity will be appreciated by a comparison of Examples 1 and 2.

Example 3

A formulation optimisation study was carried out to obtain the best combination of properties for use in inks. Materials of low resistivity and high surface area were sought. It has been found that smaller particles with high surface area do not scatter visible light as much as larger particles. Therefore a combination of high surface area (leading to better transparency when in an ink) and low resistivity is desirable.

The key variables identified were: tin content (or amount of doping); polymer content (essentially the amount of reduction); calcination temperature; and the concentration of solids in solution.

The levels of the variables studied were as follows:

Tin Content, 1%, 5% and 10% mole equivalents in ITO;
Polymer Content 1.25, 1.5 and 1.75 x mol. equivalents of $In_2(SO_4)_3$
Calcination Temperature (Tcal(°C)) 800°C, 900°C and 1000°C
Concentration of Solution 20% and 33% of indium sulphate in water.

Approximately 100g of precursor solution were prepared at each level of the formulation variables giving a total of 18 distinct solutions. Each of these was

processed as described in Example 1 except for the calcination step. At this point each of the 18 dried precursor samples was divided into three separate lots. The first lot of 18 was calcined at 800°C, the next at 900°C and finally the remainder at 1000°C. All samples had their resistivity and BET measured in accordance with Analytical Methods 1 and 2.

The data is summarised in Table 1 below.

Example 4

The formulations of Example 3.22, 3.27, 3.28, 3.32, 3.46, 3.50, 3.51 and 3.52 were selected for assessment on larger scale samples (5 times scale up; 250g samples) and such samples were prepared in accordance with the procedure in Example 1 and re-tested. The bed depth of the samples (distance "d" in Figure 7) was 50mm. Results are provided in Table 2 below.

Example 4.2 was prepared many times with similar properties and was chosen as the optimum formulation with 900°C as the calcination temperature.

To optimise properties of ITO prepared it is believed to be important to consider the bed depth in product containers. If the bed depth is high and high amounts of polymer are used and calcinations are carried out at high temperature there is a risk of scintering the primary particles and, furthermore, the properties of ITO produced may be detrimentally affected. This may be explained on the basis that reducing gases are produced from the precursor during calcinations and, consequently, the ITO towards an upper end of a bed is contacted by a greater amount of this gas than would be the case in a shallower bed. Consequently, there is a greater risk of over reduction, thereby affecting properties.

Example 5 – General Procedure for preparation of ITO precursors by precipitation

For simplicity the procedures involved in making ITO are broken down into a number of separate steps:

a) preparation of starting metal salt solution and base solutions

b) production of precursor precipitate using in-line double jet precipitation rig

Table 1

Example No	Tin (%)	Polymer (mol.equiv)	T_{cal}(°C)	Conc. (%)	Res. Ω.cm	BET (m^2/g)
3.1	1	1.25	800	20	797.3	33.3
3.2	1	1.25	800	33	676.5	29.3
3.3	1	1.25	900	20	6.57	9.8
3.4	1	1.25	900	33	7.7	13
3.5	1	1.25	1000	20	0.7	<5
3.6	1	1.25	1000	33	2	5.3
3.7	1	1.50	800	20	291.6	35.2
3.8	1	1.50	800	33	23.2	25
3.9	1	1.50	900	20	1.08	7.5
3.10	1	1.50	900	33	1.1	7
3.11	1	1.50	1000	20	0.14	<5
3.12	1	1.50	1000	33	0.2	<5
3.13	1	1.75	800	20	1.48	10.1
3.14	1	1.75	800	33	1.12	7.4
3.15	1	1.75	900	20	0.49	<5
3.16	1	1.75	900	33	0.36	<5
3.17	1	1.75	1000	20	0.18	<5
3.18	1	1.75	1000	33	0.08	<5
3.19	5	1.25	800	20	33.7	37.9
3.20	5	1.25	800	33	12.1	38.4
3.21	5	1.25	900	20	1.49	25.6
3.22	5	1.25	900	33	0.7	22.1
3.23	5	1.25	1000	20	0.21	6.5
3.24	5	1.25	1000	33	0.35	9.9
3.25	5	1.50	800	20	11.5	42.2
3.26	5	1.50	800	33	3.24	33.1
3.27	5	1.50	900	20	0.42	16.8
3.28	5	1.50	900	33	0.34	16.3
3.29	5	1.50	1000	20	0.11	<5
3.30	5	1.50	1000	33	0.2	<5
3.31	5	1.75	800	20	0.94	25.5
3.32	5	1.75	800	33	0.77	33.3
3.33	5	1.75	900	20	0.24	6.7

Example No	Tin (%)	Polymer (mol.equiv)	T_{cal}(°C)	Conc. (%)	Res. Ω.cm	BET (m^2/g)
3.34	5	1.75	900	33	0.15	<5
3.35	5	1.75	1000	20	0.07	<5
3.36	5	1.75	1000	33	0.09	<5
3.37	10	1.25	800	20	9.68	39.1
3.38	10	1.25	800	33	10.57	42.9
3.39	10	1.25	900	20	1.48	25
3.40	10	1.25	900	33	1.86	24.8
3.41	10	1.25	1000	20	0.44	<5
3.42	10	1.25	1000	33	0.36	10
3.43	10	1.50	800	20	3.33	38
3.44	10	1.50	800	33	0.98	34
3.45	10	1.50	900	20	0.21	8.4
3.46	10	1.50	900	33	0.23	12.1
3.47	10	1.50	1000	20	0.18	<5
3.48	10	1.50	1000	33	0.22	10.7
3.49	10	1.75	800	20	0.97	32.1
3.50	10	1.75	800	33	0.38	29.3
3.51	10	1.75	900	20	0.25	10.7
3.52	10	1.75	900	33	0.25	12.1
3.53	10	1.75	1000	20	0.21	27.1
3.54	10	1.75	1000	33	0.17	<5

Table 2

Example No	Similar Example	Tin (%)	Polymer (mol. equiv)	T_{cal} (°C)	Conc (%)	Res.Ω.cm	BET (m^2/g)
4.1	6.22	5	1.25	900	33	0.7	22.1
4.2	6.27	5	1.50	900	20	0.13	28
4.3	6.28	5	1.50	900	33	0.23	12.1
4.4	6.32	5	1.75	800	33	0.51	18.2
4.5	6.46	10	1.50	900	33	0.81	21.6
4.6	6.50	10	1.75	800	33	0.27	18.7
4.7	6.51	10	1.75	900	20	0.16	5
4.8	6.52	10	1.75	900	33	0.25	5

c) recovery and milling of precipitate

d) transformation of precursor precipitate to ITO by thermal treatment

Each of the aforementioned is described further below:

Step (a) Preparation of Starting Metal Salt and Base Solutions.

The composition of starting metal salt and neutralising base solutions are tailored so as to produce a reasonably concentrated but still handleable precipitated product in the pH 6-8 range when equal volumes of the metal salt and neutralising base are mixed together in the double jet precipitation rig, described hereinafter.

Step (b) Precipitation Process for Making ITO Precursor.

A block diagram of the in-line double jet precipitation apparatus employed to make the precipitated ITO precursor is provided in Figure 2.

Referring to Figure 2, thermostatically-controlled reactant feed vessels 1a and 1b are arranged to deliver, using pulseless volumetric pumps 2, reactants via feed lines 3 to a mixer element 4 and thereafter into a thermostatically-controlled receiver vessel 5 which includes a stirrer 6, thermometer 7 and pH meter 8.

Given the required metal salt and neutralising base solutions the precipitated precursor is prepared according to the following steps:

- The receiver vessel is charged with distilled water
- The two separate feed vessels are charged respectively with the metal salt and base solutions and allowed to come to thermal equilibrium prior to purging the feed lines to the mixer element with their respective metal salt and base solutions
- The volumetric displacement pumps are started simultaneously
- The precipitate is discharged into the receiver vessel which is continuously stirred
- Continuous monitoring of pH is maintained throughout the precipitation
- Pumping of the feedstock solutions is terminated when either metal salt or base solutions have been consumed and before air becomes entrained in the volumetric pumps

- On completion of the precipitation if the pH of precipitate in the receiver vessel has drifted outside the desired pH 6-8 range it is re-adjusted to lie in pH 6-8 by appropriate addition of sulfuric acid or ammonium hydroxide solution

- The precipitate in the receiver vessel is aged for a specified time prior to recovery

The preferred conditions for the precipitation process at the laboratory scale are as outlined below:

Precipitation Conditions

Feedstock temperature	Room Temperature (~20°C)
In-line Mixer ID	0.5mm
Flow Rate(each feed)	ca 50ml.min^{-1}
Flow Rate(Total)	100ml.min^{-1}
Volume of distilled water in receiver	1/5 total volume of metal salt and base solutions
Product pH range	pH 6 to pH 8
Precipitate ageing	15 to 30 minutes after completion of the precipitation

Step (c) (i) Precipitate Filtration and Washing

The precipitate is filtered under vacuum using a Buchner apparatus fitted with ashless filter papers. The filter cake is washed with at least 3 wash volumes of water adjusted to pH8-9 with ammonium or sodium hydroxide. The conductivity of the filtrate is monitored. Washing is deemed to be satisfactory when the filtrate conductivity is < 450microS.cm^{-1}.

The filter cake, containing approximately 40%w/w solids, is then dried in an air oven according to the conditions outlined below:

Drying Conditions

Temperature	80 to 100°C
Time at temperature	18 to 20 hours.

Step (c) (ii) Milling

The product is milled by hand using a mortar and pestle.

Step (d) Calcination

The dried and milled precipitate in powder form is loaded into silica crucibles to a bed depth of approximately 2cm. The crucibles are transferred to a preheated furnace with suitably extracted exhaust and left at elevated temperature for the appropriate time. The crucible is withdrawn from the furnace and the contents immediately quenched by tipping onto a steel tray or allowed to slow cool in air.

Calcination Conditions

Temperature	900 to 1000°C
Time at Temperature	30minutes
Atmosphere	Air
Bed depth	~2cm

Example 6 (comparative) and Example 7

The procedure of Example 5 was followed using Indium (III) chloride (InCl3) which was neutralised using sodium hydroxide. Example 7 was precipitated in the presence of Dispex GA40 (a polyacrylic acid). In this regard, a 1%wt solution of Dispex GA40 was prepared and added to the sodium hydroxide feed stream prior to mixing.

A general equation for the neutralisation is given below:

$$InCl_3 : Sn + 3NaOH \rightarrow In(OH)_3 : Sn + 3NaCl$$

Tin is incorporated into the oxide lattice at 5 atom percent. The stoichiometry of the reaction is controlled to allow regulation of the precipitation pH. The composition of starting metal salt and neutralising base solutions are tailored so as to produce a reasonably concentrated but still handleable precipitated product in the pH 6-8 range when equal volumes of the metal salt and neutralising base are mixed together in the double jet precipitation rig.

For 5atom% tin doped ITO the required solution concentrations are as outlined below:

Mixed Metal Salt Solution	$[InCl_3]$ = 0.475molar, $[SnSO_4]$ = 0.05molar
Base	2.95molar NaOH

The base solution is made up by dilution of concentrated sodium hydroxide standardised by titration against an acid standard. To make up the metal salt solution the appropriate amounts of indium(III) chloride and tin(II) chloride powders are mixed together. These are then added with stirring to distilled water and finally made up to the volume necessary to achieve the desired concentration. Some heating may be required to fully dissolve the metal salts. The reactive precipitation may be represented by the equation below:

$$0.95InCl_3 + 0.05SnCl_4 + 3.05NaOH \rightarrow In(OH)_x : Sn(OH)_y \downarrow + 3.05NaCl$$

The data in Table 3 below details the powder resistivity obtained at highest volume fraction to illustrate the effect of with and without polymer addition on the powder resistivity.

Table 3

Example	Calcination Conditions			Other treatment	Resistivity ohm.cm	Powder Vol Fraction %
6	1000	air	30min	Steel quench	0.43	24.79
7	1000	air	30min	Steel quench	0.07	34

Example 8

The following formulation was prepared by using the method of Example 1 as far as the freeze drying stage. Calcination was carried out as follows: alumina trays were used to hold the precursor for the calcination step. 50g of precursor was placed in each tray and placed on the belt of a tunnel furnace which consisted of three zones. In the first zone, there was no heating; the product passes into this zone via a nitrogen curtain. The product then enters the hot zone which is a metal muffle controlled at 900°C and a cover gas of nitrogen 112 is used. Exhaust gases are removed via a venturi. After the heating zone the product tray passes into a cooling zone using circulating water to remove heat from the product. Nitrogen is again used as a cover gas. Typically, the total distance of the three zones is 3.4m with the hot zone being 1.4m. The belt speed is 5cm/minute. The product ITO emerges from the cooling zone below 50°C and can be transferred directly to containers.

The powder properties were assessed in accordance with Analytical Methods 1 and 2.

Indium(III) Sulphate	575g (1.11 mol)
Ammonium Sulphate	147.5g (1.11 mol)
Tin(II) Sulphate	25g (0.12 mol)
Polacrylamide Solution	86g (1.34 mol.equiv)
Water	2400g (133.3 mol)

The powder resistivity was 0.25 Ω.cm at a powder volume of 25%. The BET surface area was 15 m^2/g.

Example 9

Samples (A series) of EL lamps were prepared using the ITO prepared as described in Example 8, while a second, comparative set (B series) were prepared using the ITO L-1469-2, commercially available from Mitsubishi. The results of testing on these samples are shown in Table 4.

Table 4

Sample	Light Output (Cd/m2)	Amperage Draw (Milliamps)	Colour-Co(x-y)[1]	LAR[2]
A1	90.5	3.21	0.202-0.475	28.19315
A2	95.2	3.31	0.202-0.475	28.76133
A3	94.7	3.30	0.202-0.476	28.69697
B1	28.2	1.28	0.193-0.433	22.03125
B2	34.1	1.30	0.193-0.432	26.23077
B3	31.2	1.26	0.192-0.432	24.76190

[1] – Measured using the 1931 CIE standard.

[2] – LAR is light output divided by amperage draw.

As shown in Table 4, the EL lamps containing the indium tin oxide of the present invention provide superior light output and other properties than the EL lamps containing the commercially available indium tin oxide.

Claims

1. A method of preparing ITO which includes the step of calcining a precursor material which includes a source of indium, a source of tin and an oxygen scavenging means.

2. A method according to claim 1, wherein said oxygen scavenging means is a chemical means.

3. A method according to claim 1 or claim 2, wherein said oxygen scavenging means or a decomposition product thereof forms covalent bonds with products or intermediates produced by decomposition of compounds included in said precursor material.

4. A method according to any preceding claim, wherein said oxygen scavenging means is arranged to form SO_2 from decomposition products produced during calcination; and/or to produce CO_2 from decomposition products produced during calcination; and/or to produce water from decomposition products produced during calcination.

5. A method according to any preceding claim, wherein said oxygen scavenging means is arranged to decompose during calcination.

6. A method according to any preceding claim, wherein said oxygen scavenging means is an organic polymeric material.

7. A method according to any preceding claim, wherein said oxygen scavenging means comprises a polymeric material which includes a repeat unit which consists of atoms selected only from carbon, hydrogen, oxygen and nitrogen atoms.

8. A method according to any preceding claim, wherein said oxygen scavenging means is water soluble.

9. A method according to any preceding claim, wherein said oxygen scavenging means is an acrylamide.

10. A method according to any preceding claim, wherein the amount of scavenging means in said formulation is 0.9 to 2 times the amount required to fully reduce the products of the decomposition of the source of indium to indium oxide.

11. A method according to any preceding claim, wherein said precursor material is prepared in a process which involves hydrolysis, precipitation or cryogenic processing of compounds arranged to produce said precursor material.

12. A method according to claim 11, wherein said precursor material is prepared by hydrolysis or precipitation and is a hydroxide.

13. A method according to any preceding claim, wherein the ITO produced in the method has a powder resistivity in the range 0.1 to 0.5 Ω.cm.

14. A method according to any preceding claim, wherein the step of calcining said precursor material includes subjecting to said precursor material to a temperature of at least 400°C.

15. A method according to claim 14, wherein said temperature is at least 600°C and is less than 1200°C.

16. A method according to claim 11, wherein said process includes a cryogenic process which includes the steps of:

(a) causing a liquid formulation which includes a solvent to form a solid, wherein the formulation includes:

(i) an indium compound, a tin compound and ammonium sulphate; or

(ii) $(NH_4)In(SO_4)_2$ and a tin compound.

17. A paint, ink or resin comprising ITO prepared as described in any of claims 1 to 16.

18. An electroluminescent lamp comprising ITO made by the method according to any one of claims 1 to 16.

19. A method, indium tin oxide, a paint, ink or resin and an electroluminescent lamp, each being independently substantially as hereinbefore described with reference to the examples.

Fig.1.

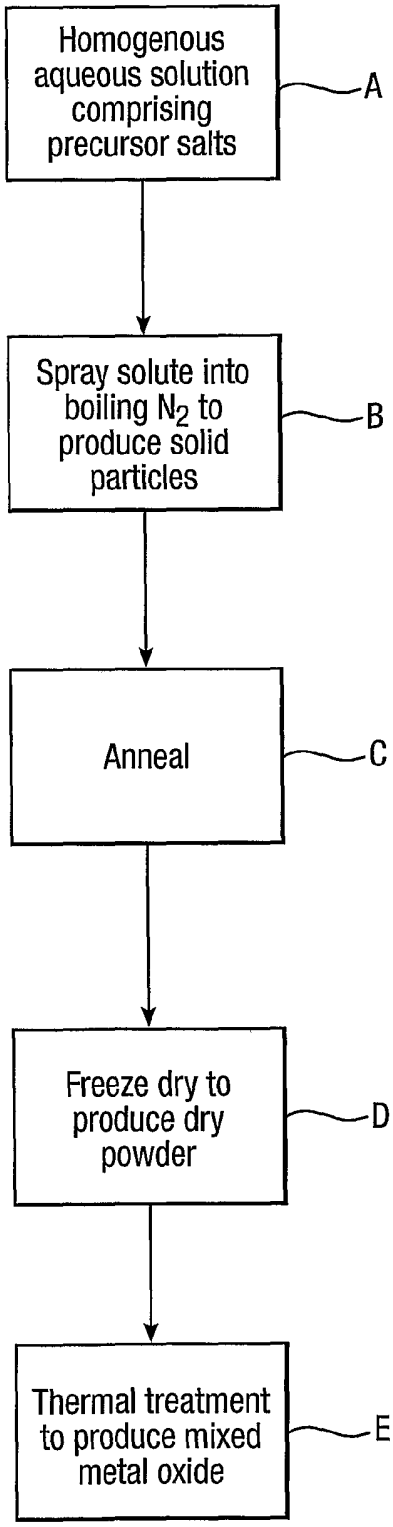

Homogenous aqueous solution comprising precursor salts
A
Spray solute into boiling N_2 to produce solid particles
B
Anneal
C
Freeze dry to produce dry powder
D
Thermal treatment to produce mixed metal oxide
E

Fig.2.

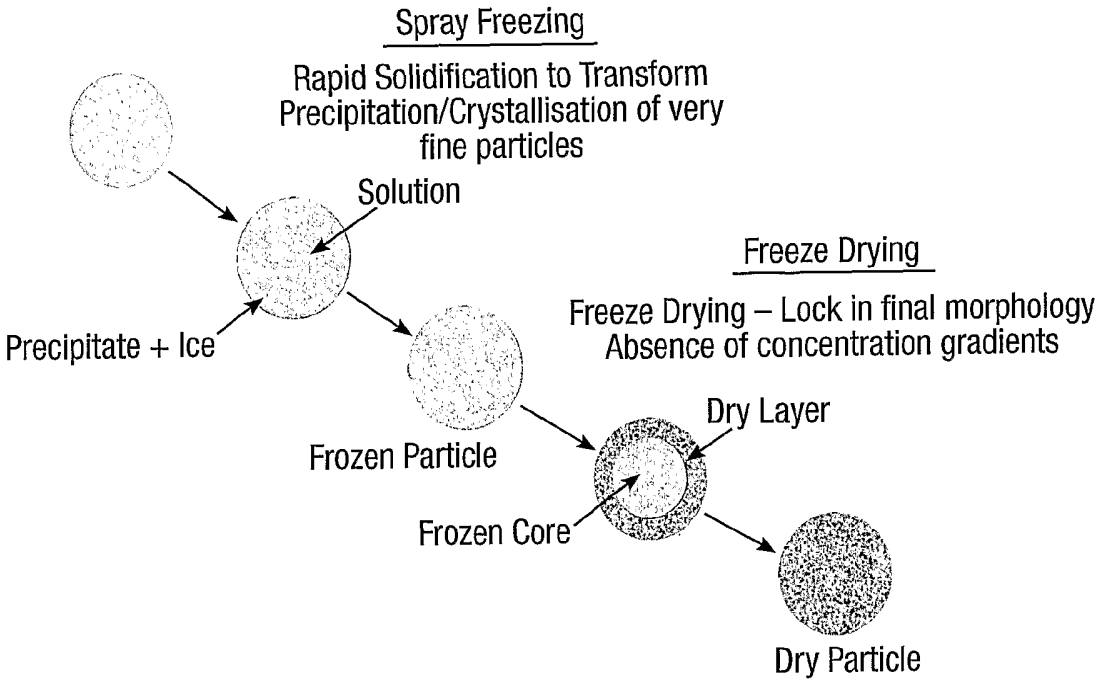

Spray Freezing
Rapid Solidification to Transform Precipitation/Crystallisation of very fine particles
Solution
Precipitate + Ice
Freeze Drying
Freeze Drying – Lock in final morphology
Absence of concentration gradients
Frozen Particle
Dry Layer
Frozen Core
Dry Particle

Fig.3.

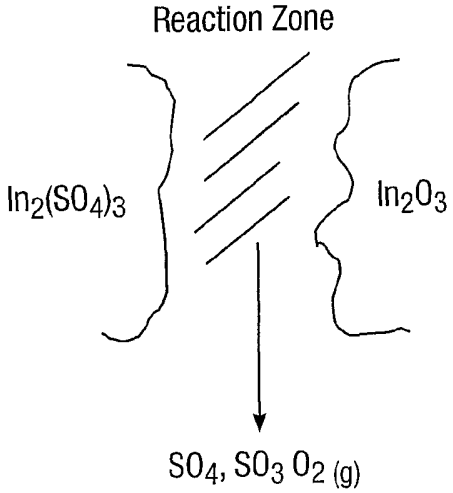

Reaction Zone
$In_2(SO_4)_3$
In_2O_3
SO_4, SO_3 $O_{2\ (g)}$

Fig.4a.

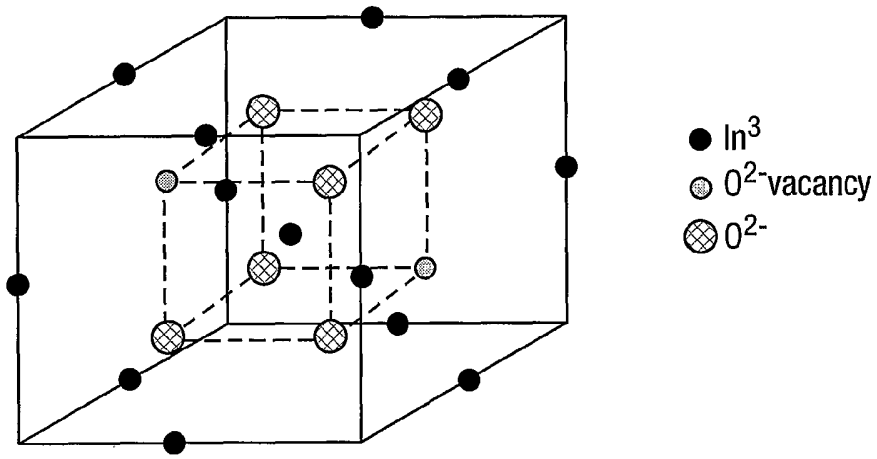


Fig.4b.

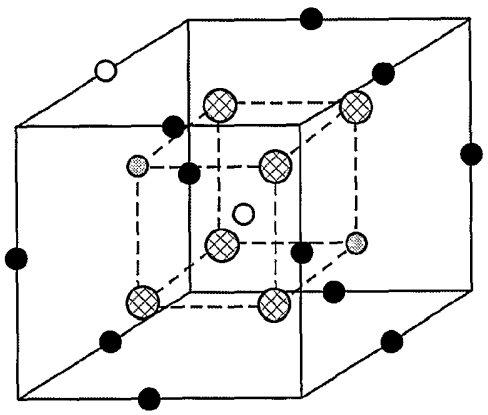


Fig.4c.

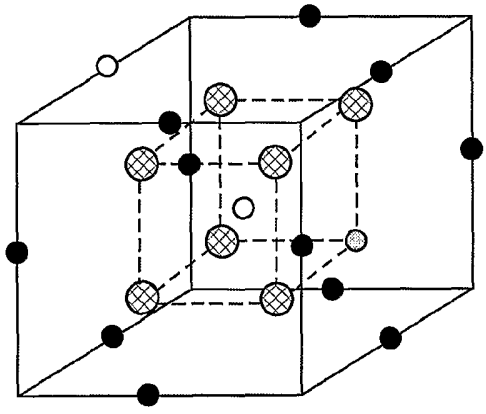


Fig.5.

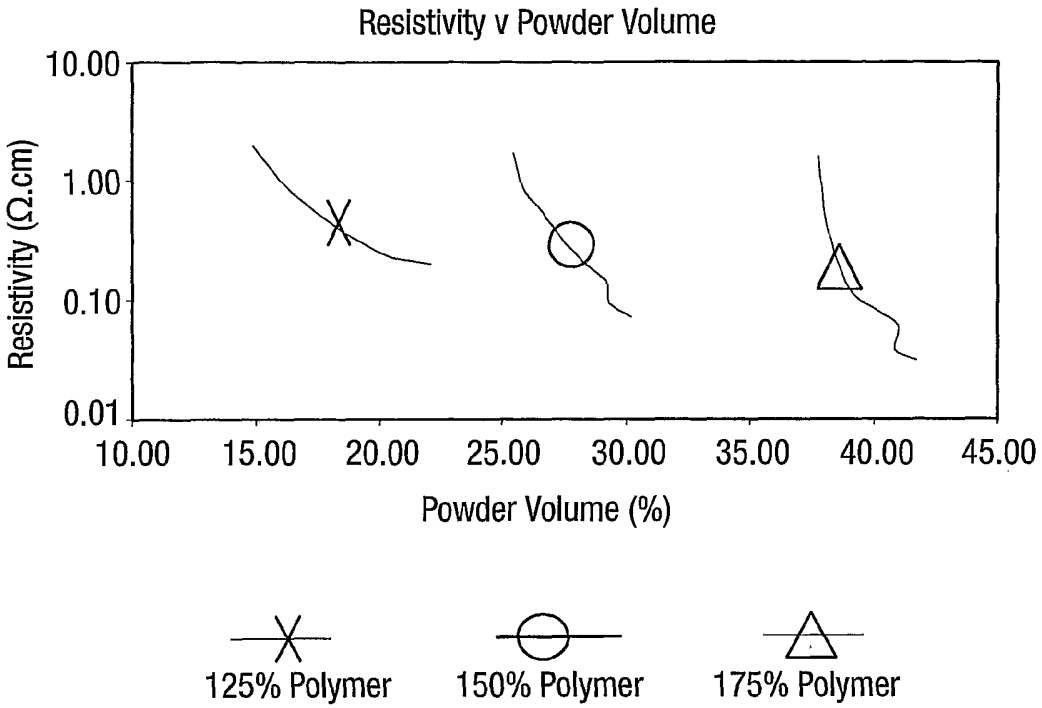

Resistivity v Powder Volume
10.00
1.00
0.10
0.01
Resistivity (Ω.cm)
10.00
15.00
20.00
25.00
30.00
35.00
40.00
45.00
Powder Volume (%)
125% Polymer
150% Polymer
175% Polymer

Fig.6.

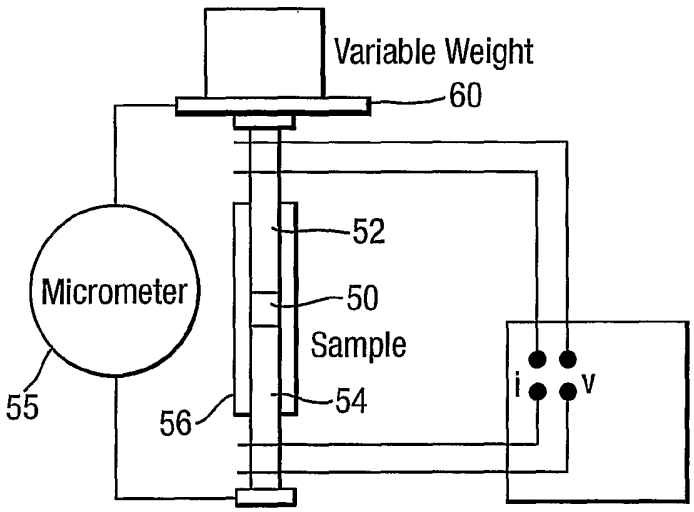

Variable Weight
60
52
50
Sample
54
Micrometer
55
56
i
v

Fig.7.

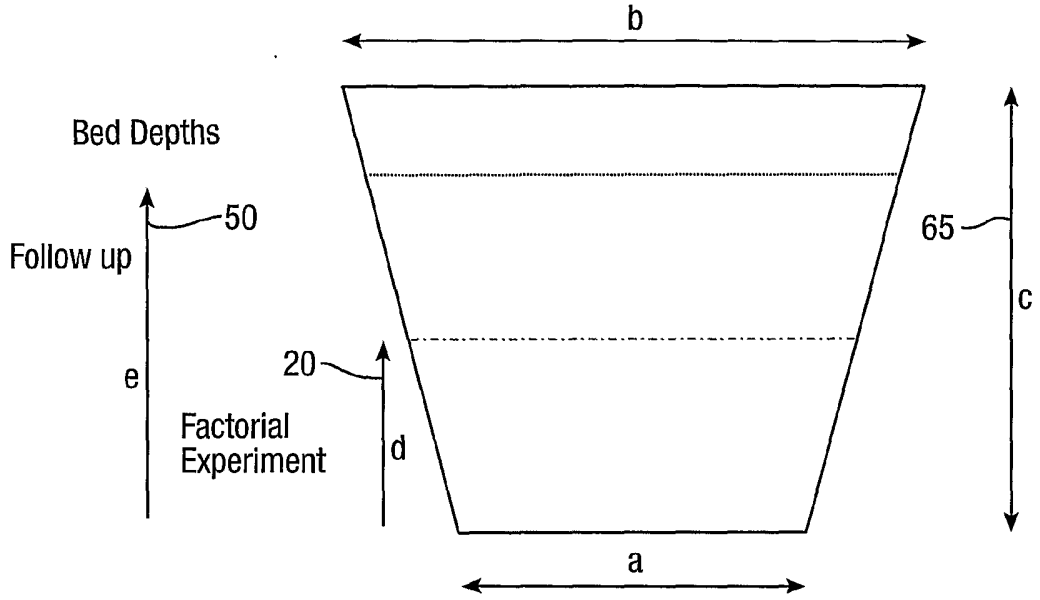
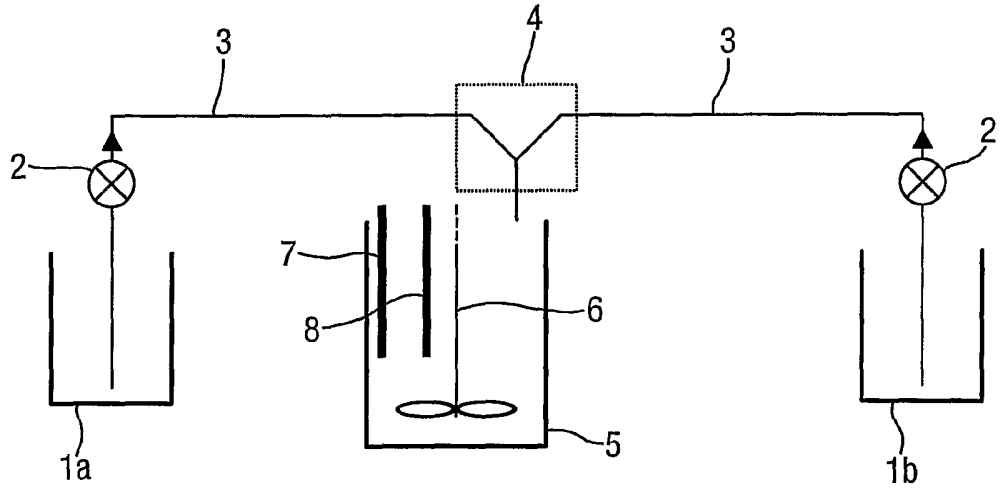

b
Bed Depths
50
Follow up
e
20
Factorial
Experiment
d
65
c
a

Fig.8.


3
4
3
2
2
7
8
6
5
1a
1b

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB2005/002056

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C01G19/00 C09C1/00 C01B13/18

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C01G C09C C01B

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)
EPO-Internal, WPI Data, INSPEC

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 533 966 B1 (NONNINGER RALPH ET AL) 18 March 2003 (2003-03-18) column 4, line 31 - column 7, line 21 column 7, lines 43-57 column 11, lines 9-15 column 12, lines 27-53 -----	1-8, 10-15, 17-19
X	US 5 744 118 A (IMAMURA ET AL) 28 April 1998 (1998-04-28) column 1, line 45 - column 2, line 53 column 3, line 64 - column 5, line 54 column 11, lines 28-67 example 4 ----- -/--	1-15,19

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

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Date of the actual completion of the international search	Date of mailing of the international search report
10 August 2005	18/08/2005

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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