

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
15 December 2005 (15.12.2005)

PCT

(10) International Publication Number
WO 2005/118478 A1

(51) International Patent Classification⁷: **C01G 19/00**,
C01B 13/18, C09C 1/00

(21) International Application Number:
PCT/GB2005/002063

(22) International Filing Date: 24 May 2005 (24.05.2005)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0411883.2 28 May 2004 (28.05.2004) GB

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, YU, ZA, ZM, ZW.

(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: INDIUM TIN OXIDE

(57) Abstract: A method of preparing indium tin oxide (ITO) is described which involves calcining a precursor material, for example indium hydroxide or indium ammonium sulphate and subjecting the calcined material which is at a first elevated temperature to a cooling process in which it is cooled rapidly, for example at a rate of greater than 45 °C per second, down to a temperature of 350 °C or below.

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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*.

- 5 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 of properties, including antistatic, anti rusting/corrosion, electric field/electromagnetic
- 10 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
- 15 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

20 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 $\Omega/\square$ 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

25 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

30 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. US6096285 describes calcination of co-precipitated hydroxides of indium and tin.

This invention is based on the discovery of an advantageous process for improving the properties of ITO that may be used after calcination of a precursor material adapted to produce ITO.

It is an object of the present invention to provide a process for producing ITO that 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 steps of:

- 15 (A) calcining a precursor material which includes a source of indium and a source of tin to produce a calcined material; and
- (B) (i) subjecting the calcined material which is at a first elevated temperature to a cooling process in which it is cooled or allowed to cool to a temperature of less than 500°C (preferably less than 400°C, more preferably less than 20 350°C) in an atmosphere which includes less than 5wt% oxygen; and/or
- (B) (ii) subjecting the calcined material which is at a first elevated temperature to a cooling process wherein it cools from said first elevated temperature to a temperature which is 100°C less than said first elevated temperature in less than 5 seconds (preferably less than 2 seconds, more preferably less than 1 25 second); and/or
- (B) (iii) subjecting the calcined material which is at a first elevated temperature to a cooling process wherein it cools from said first elevated temperature to 350°C at a rate of greater than 45°C/second (preferably greater than 90°C/second, more preferably greater than 225°C/second).
- 30 Without being limited by this statement, it is believed that calcination of said precursor material creates oxygen vacancies in the crystal lattice of the ITO which has the net effect of increasing the number of free electrons in the valence band

causing an increased in ITO particle conductivity. However, formation of oxygen vacancies is believed to be an equilibrium effect and, consequently, if the particles are exposed to an oxygen containing environment, recombination of oxygen with the vacant lattice sites occurs thus reducing conductivity. By cooling the calcined ITO in an atmosphere having a reduced amount or no oxygen and/or cooling the material relatively rapidly, it has been found that conductivity is advantageously improved which is believed to be due to the reduced availability in the region of the calcined ITO of oxygen and therefore reduced filling of oxygen vacancies in the ITO.

When step (B)(i) is carried out, said calcined material is preferably subjected to a said atmosphere as described for the entirety of the cooling process from said first elevated temperature to a said temperature less than 500°C, 400°C, 350°C as applicable.

In step (B)(i), said atmosphere may include less than 4wt%, suitably less than 2wt%, preferably less than 1 wt%, more preferably less than 0.5wt%, especially less than 0.1wt%, oxygen. The amount of oxygen may be of the order 100ppm or even less than 10ppm.

Preferably, in step (B)(i), said atmosphere comprises a non-oxidizing gas. Such a gas is suitably unable to react with the calcined material. Said atmosphere suitably comprising at least 60wt%, preferably at least 75wt%, more preferably at least 90wt%, especially at least 95wt% of a said non-oxidising gas. Said atmosphere could include one or more non-oxidizing gases. For example, said atmosphere could include an inert gas (e.g. 96 to 99.9wt% thereof) and a reducing gas (e.g. 0.1 to 4wt% thereof). A preferred non-oxidizing gas is an inert gas that may be selected from noble gases and nitrogen. A preferred inert gas is nitrogen. Suitably, said atmosphere of step (B)(i) includes at least 85wt%, preferably at least 90wt%, more preferably at least 95wt% nitrogen. Said atmosphere may consist essentially of nitrogen.

Step (B)(i) may include positioning the calcined material, suitably in a receptacle, in a confined space that contains said atmosphere for example nitrogen gas.

Steps (B)(ii) and (iii) may be carried out in various ways. In a first embodiment, the method may involve contacting the calcined material which is at a first elevated temperature with a solid, liquid or gas which has a thermal conductivity at 25°C and atmospheric pressure (or, if the thermal conductivity cannot be measured under said

conditions, the thermal conductivity of the solid, liquid or gas under the conditions of initial contact with said calcined material) of $1 \text{ Wm}^{-1}.\text{K}^{-1}$ or greater, in order relatively rapidly to remove heat from the calcined material. Suitably, the thermal conductivity of said solid, liquid or gas, measured as aforesaid, is at least 5, preferably at least 10, more preferably at least 15. At the time of initial contact with said calcined material, the solid, liquid or gas is suitably at a temperature of less than 100°C , preferably less than 60°C , more preferably less than 40°C , especially at ambient temperature or below. Preferably, in the method, the calcined material is deposited in/on the solid, liquid or gas. It is preferably transferred from a receptacle in/on which it is calcined into/on the solid, liquid or gas in which it is cooled. Preferably in accordance with said first embodiment, said calcined material is contacted with a solid which is preferably a metal and may be a steel. Said solid may be in the form of a carrier, for example a receptacle, into or on which the calcined material may be placed. Initial contact with the solid may effect crash cooling of the calcined material. The carrier is preferably upwardly open to facilitate loss of heat from the calcined material to the surroundings. Also, the calcined material may be arranged on the carrier so that it is spread substantially evenly thereon to facilitate heat transfer from the calcined material to both the carrier and the environment.

In a second (less preferred) embodiment, the method may involve immersing the calcined material in a liquid which is at a temperature of less than 250°C , preferably less than 100°C , more preferably less than 50°C . The liquid could be a liquefied gas, for example nitrogen, or it could be a material which is a liquid at STP, for example water. The liquid is preferably at ambient temperature or below when initially contacted with said calcined material.

The method of the first aspect could involve step (B)(i) in combination with (B)(ii) and/or (B)(iii).

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 and causing hydrolysis or precipitation of the salts, preferably by addition of acid or base. The hydrolysis product or precipitate 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:

- 5 (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) $(\text{NH}_4)\text{In}(\text{SO}_4)_2$ and a tin compound.

- 10 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.

- 15 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.

- 20 Step (a) preferably includes causing the liquid formulation to cool, suitably to a temperature which 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
- 25 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.

- 30 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%).

- 5 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 $(\text{NH}_4)\text{In}(\text{SO}_4)_2$ (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.

- 10 If said liquid formulation includes more than one type of indium compound or more than one type of tin compound, the abovementioned 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.

- 15 Preferably, the indium compound and ammonium sulphate of step (a)(i) are adapted to produce $(\text{NH}_4)\text{In}(\text{SO}_4)_2$. Thus, the compounds of (a)(i) may upon contact and/or reaction therebetween produce the compounds of (a)(ii).

Each of the compounds of step (a)(i) and (ii) selected for treatment in step (a) are preferably in solution in said liquid formulation.

- 20 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 $(\text{NH}_4)\text{In}(\text{SO}_4)_2$, and frozen solvent, especially water, included initially in said liquid formulation of step (a).

- 25 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).

- 30 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.

- 5 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
- 10 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
- 15 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
- 20 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.

- 25 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
- 30 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

- 5 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 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.

- 15 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 $\Omega\cdot\text{cm}$, more preferably in the range 0.2 to 0.5 $\Omega\cdot\text{cm}$ measured at less than 30% volume fraction, more preferably when measured at less than 25% volume fraction.

- 20 The BET surface area may be less than 35m²/g, suitably less than 30m²/g, preferably less than 25m²/g, more preferably less than 20m²/g, especially 17m²/g or less. The BET surface area may be at least 10m²/g.

The invention extends to a paint, ink or resin comprising ITO as described in any preceding aspect

- 25 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
30 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 a block diagram of an in-line double jet precipitation apparatus for making precipitated ITO precursors;

Figure 3 is a graph of temperature vs time during cooling of samples;

Figure 4 is a schematic representation of a crucible;

Figure 5 is a schematic representation of a continuous belt furnace; and

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

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 $\text{In}_2(\text{SO}_4)_3$, ammonium sulphate and

SnSO₄; (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.

As illustrated hereinafter, it has been determined that it is possible to reduce the powder resistivity of the ITO produced after calcination by relatively rapid cooling of the product from its high calcination temperature. This may be achieved by transferring the hot calcined product to a metal plate or into liquid nitrogen. Little discernible differences in particle morphology is observed but powders with relatively low resistivities may be obtained.

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 of 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 to be tested is first weighed and inserted between two pistons held in place with a glass sleeve. A micrometer is used to measure the position of a ram 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_c 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 the material is.

5 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.

- 10 In each of the following examples which involve calcinations in air, a frusto-conical crucible as shown in Figure 4 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 the Examples, unless otherwise stated.

- 15 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 – 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:

- 20 a) preparation of starting metal salt solution and base solutions
- b) production of precursor precipitate using in-line double jet precipitation rig
- c) recovery and milling of precipitate
- d) transformation of precursor precipitate to ITO by thermal treatment

Each of the aforementioned is described further below:

- 25 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.

5 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.

10 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
- 15 • 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
- 20 • 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
- 25 • 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

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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

- 5 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:

10 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

- 15 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.

20 Calcination Conditions

Temperature	900 to 1000°C
Time at Temperature	30minutes
Atmosphere	Air

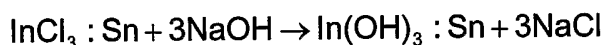
Bed depth

~2cm

Example 2 – Preparation of specific ITO precursors

The procedure of Example 1 was followed, to prepare Example 2.1, using indium (III) chloride (InCl_3) which was neutralised using sodium hydroxide.

- 5 A general equation for the neutralisation is given below:

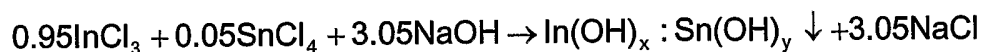


- 10 Tin is incorporated into the oxide lattice at 5 atom percent. The stoichiometry of the reaction is controlled to allow regulation of the precipitation pH. The composition of starting metal salt and neutralising base solutions are tailored so as to produce a reasonably concentrated but still handleable 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	$[\text{InCl}_3] = 0.475\text{molar}$, $[\text{SnSO}_4] = 0.05\text{molar}$
Base	2.95molar NaOH

- 15 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
- 20 heating may be required to fully dissolve the metal salts. The reactive precipitation may be represented by the equation below:



- Example 2.2 involves making up a metal salt solution comprising the appropriate amounts of indium (III) sulphate and tin (II) sulphate powders. The powders are
- 25 mixed together and are added with stirring to distilled water and then made up to the volume necessary to achieve the desired solution concentration. Since the

dissolution process is moderately exothermic it may be necessary to warm the mixture to 50°C to effect complete dissolution.

Example 2.3 is another batch prepared as described for Example 2.1

Example 3 – Calcination of ITO precursors

- 5 The ITO precursors prepared in Example 2 were subjected to a thermal treatment which comprised calcination in air in a furnace at a temperature of 900°C or of 1000°C and ambient pressure for a period of 30 minutes. After calcination, the ITO samples prepared were treated according to either the Method 3.1, 3.2 or 3.3 procedures, described below.

10 Method 3.1

This “quench cool” method involved tipping calcined material onto a steel tray and spreading the material as a thin layer.

Method 3.2

- 15 This “slow cool” method involved the material, in the crucible in which it is calcined, being allowed to cool in ambient air.

Method 3.3

The crucible is withdrawn from the furnace and the contents immediately quenched by tipping into a vessel containing liquid nitrogen, thereby allowing the powder to cool at the required rate.

- 20 Results and details of conditions used are provided in Table 1 below.

It will be appreciated from the results in Table 1 that the use of active cooling as in Methods 3.1 and 3.3 result in the production of lower resistivity ITO compared to use of passive cooling as in Method 3.2, for otherwise identical samples (compare Example 3a with Example 3b; and Examples 3d to 3f with one another).

25 Example 4 – assessment of cooling rates

The rate of cooling of materials of the type described above was determined. This involved measuring the time taken for a sample to cool from the calcination temperature to 260°C and, thereafter, the cooling rate was monitored using infrared

detection. Results are provided in Table 2 below and in Figure 3. The Figure 3 includes results (Examples 4.1 and 4.2) for quench cooling in accordance with Method 3.1; and two "fast cool" examples (Examples 4.3 and 4.4) wherein calcined powder samples (at 900 and 1000°C respectively) were tipped onto steel plates but not spread into thin layers; results which show the cooling rate of empty crucibles from 900 and 1000°C respectively (Examples 4.5 to 4.7); and results for slow cooling of samples from 900 and 1000°C respectively in ambient air.

Table 2 below details the time taken for some of the samples to cool from the calcination temperatures to 260°C.

10 Table 1

Example No	ITO precursor used (Example No.)	Calcination conditions			Additional treatment method	Resistivity (ohm.cm)	Powder volume fraction (%)
		Temp (°C)	Atmosphere	Time (mins)			
3a	2.1	900	Air	30	3.1	0.6	36.81
3b	2.1	900	Air	30	3.2	1.75	40.75
3c	2.2	1000	Air	30	3.1	0.23	31.25
3d	2.3	1000	Air	30	3.1	0.55	28.3
3e	2.3	1000	Air	30	3.3	0.34	27.79
3f	2.3	1000	Air	30	3.2	1.33	28.05

Table 2

Example No.	Time to cool to 260°C (seconds)
4.1	<2
4.2	<2
4.3	12
4.4	26
4.8	228
4.9	274

Example 5 – Preparation of ITO by cryogenic method (Comparative example)

Anhydrous indium(III) sulfate (57.5g, 0.111 mol) was slowly added with agitation to demineralised water (240g, 13.3 mol) at ambient temperature. Ammonium sulphate (14.75g, 0.111 mol) and tin(II) sulfate (2.5g, 0.012 mol) were subsequently added.

5 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 which 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
10 recovered. A narrow frozen particle size distribution with no particles below 100 μm was produced.

The frozen droplets were placed onto trays which 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.

15 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
20 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
25 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 allowed to cool to ambient temperature. It was observed that the initially white precursor was green after
30 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 17.7 Ω .cm and the powder volume fraction was 25.8%. The BET surface area, measured in accordance with Analytical Method 2, was 12 m²/g.

Example 6

- 5 The same formulation and procedure as described in Example 5 was used except that at the end of the calcination step the powder was quenched by discharging the hot powder from the muffle furnace directly onto a metal tray at room temperature. The resistivity and powder volume were 5.3 Ω .cm and 21.1% respectively.

10 It will be appreciated by comparing Examples 5 and 6 that the resistivity is reduced as a result of quenching in accordance with Example 6.

Example 7 – Preparation of ITO by cryogenic method

The formulation shown in Table 3 was prepared by using the method of Example 5 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
15 placed in each tray 100 (Figure 5) and placed on the belt 102 of a tunnel furnace 104 which consisted of three zones, as shown in Figure 5. In the first zone 106 there was no heating; the product passes into this zone via a nitrogen curtain 108. The product then enters the hot zone 110 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 114. After the
20 heating zone the product tray passes into a cooling zone 116 using circulating water to remove heat from the product. Nitrogen 118 is again used as a cover gas. Typically, distance x is 3.4m, distance y is 1.4m and the belt speed is 5cm/minute. The product ITO emerges from the cooling zone 116 below 50°C and can be transferred directly to containers.

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

The powder resistivity was 0.25 Ω .cm at a powder volume of 25%. The BET surface area was 15 m²/g.

30 It will be appreciated from Example 7 that very low resistivity material can be prepared by cooling in an inert atmosphere and/or by cooling relatively rapidly.

Table 3

Indium(III) Sulphate	575g (1.11mol)
Ammonium Sulphate	147.5g (1.11 mol)
Tin(II) Sulphate	25g (0.012 mol)
Polacrylamide Solution	86g (1.34 mol.equiv)
Water	2400g (133.3 mol)

Example 8

5 Samples (A series) of EL lamps were prepared using the ITO prepared as described in Example 7, 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/m ²)	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.

10 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

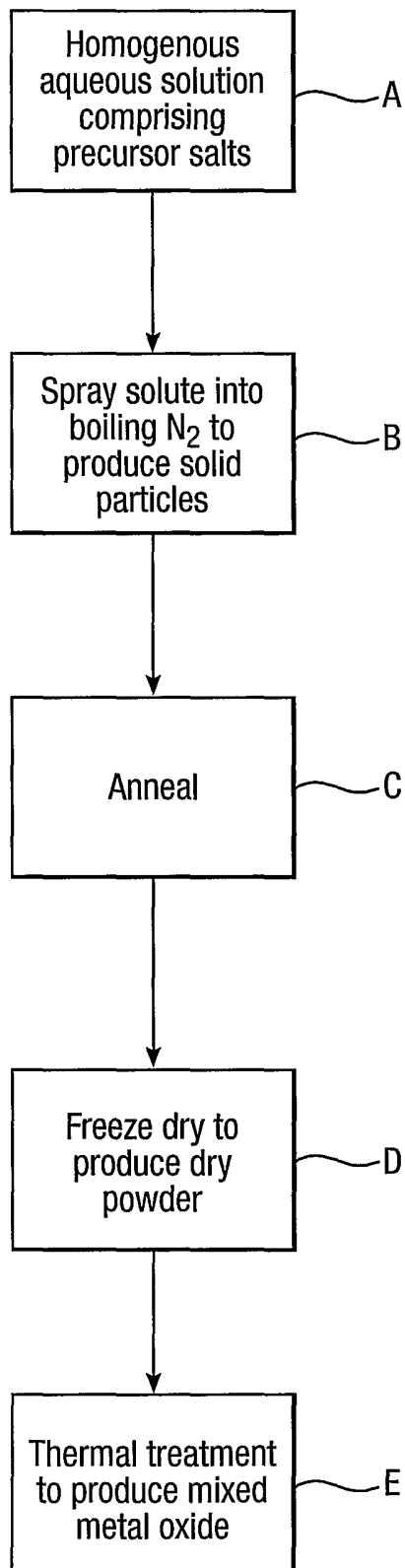
1. A method of preparing indium tin oxide (ITO) which includes the steps of:
 - (A) calcining a precursor material which includes a source of indium and a source of tin to produce a calcined material; and
 - 5 (B) (i) subjecting the calcined material which is at a first elevated temperature to a cooling process in which it is cooled or allowed to cool to a temperature of less than 500°C in an atmosphere which includes less than 5wt% oxygen; and/or
 - 10 (B) (ii) subjecting the calcined material which is at a first elevated temperature to a cooling process wherein it cools from said first elevated temperature to a temperature which is 100°C less than said first elevated temperature in less than 5 seconds; and/or
 - 15 (B) (iii) subjecting the calcined material which is at a first elevated temperature to a cooling process wherein it cools from said first elevated temperature to 350°C at a rate of greater than 45°C/second.
2. A method according to claim 1, wherein in (B)(i) the calcined material is subjected to a cooling process in which it is cooled or allowed to cool to a temperature of less than 350°C in an atmosphere which includes less than 5wt% oxygen.
- 20 3. A method according to claim 1 or claim 2, wherein in (B)(ii) the calcined material is subjected to a cooling process wherein it cools from said first elevated temperature to a temperature which is 100°C less than said first elevated temperature in less than 1 second.
- 25 4. A method according to any preceding claim, wherein said calcined material is subjected to a cooling process wherein it cools from said first elevated temperature to 350°C at a rate of greater than 225°C/second.
5. A method according to any preceding claim, wherein, in steps (B)(i) said atmosphere includes less than 0.1wt% oxygen.
- 30 6. A method according to any preceding claim, wherein, in step (B)(i), said atmosphere comprises at least 60wt% of a non-oxidising gas.

7. A method according to claim 6, wherein said non-oxidising gas is an inert gas.
8. A method according to claim 6 or claim 7, wherein said non-oxidising gas is nitrogen.
9. A method according to any preceding claim, wherein in (B)(ii) and (iii) the
5 calcined material which is at a first elevated temperature is contacted with a solid, liquid or gas which has a thermal conductivity at 25°C and atmospheric pressure of 1Wm⁻¹.K⁻¹ or greater.
10. A method according to claim 9, wherein said calcined material is contacted with a solid which is a metal.
- 10 11. A method according to any of claims 1 to 9, wherein steps (B)(ii) and (iii) are carried out by immersing the calcined material in a liquid which is at a temperature of less than 250°C.
12. A method according to any preceding claim, wherein said precursor material is prepared in a process which involves hydrolysis, precipitation or cryogenic
15 processing of compounds arranged to produce said precursor material.
13. A method according to any preceding claim, wherein said precursor material is indium hydroxide.
14. A method according to any of claims 1 to 12, wherein said process for preparing said precursor material comprises a cryogenic process which
20 includes the step 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
 - 25 (ii) (NH₄)In(SO₄)₂ and a tin compound.
15. A paint, ink or resin comprising ITO prepared in a method according to any preceding claim.
16. An electroluminescent lamp comprising ITO made by the method according to any one of claims 1 to 14.

17. 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.

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Fig. 1.



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Fig.2.

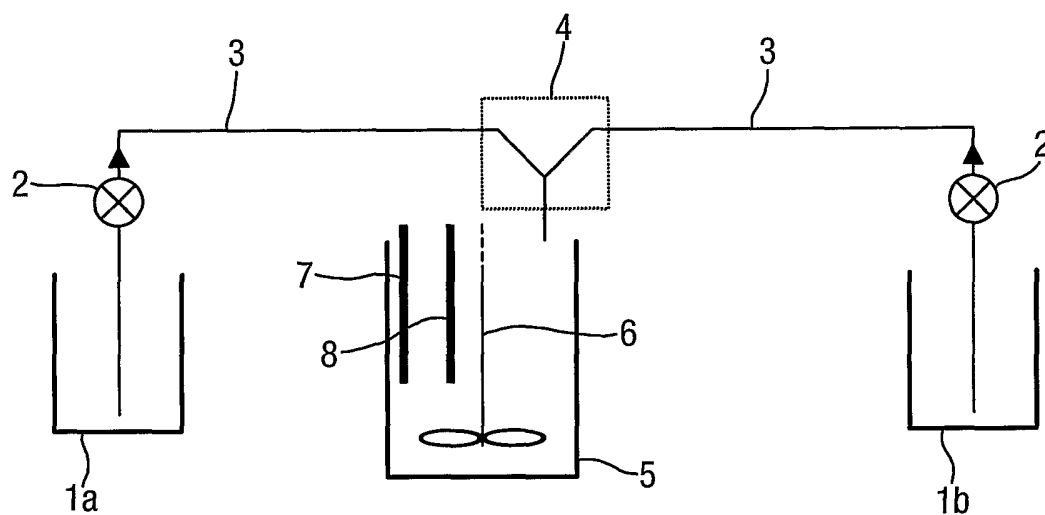


Fig.3.

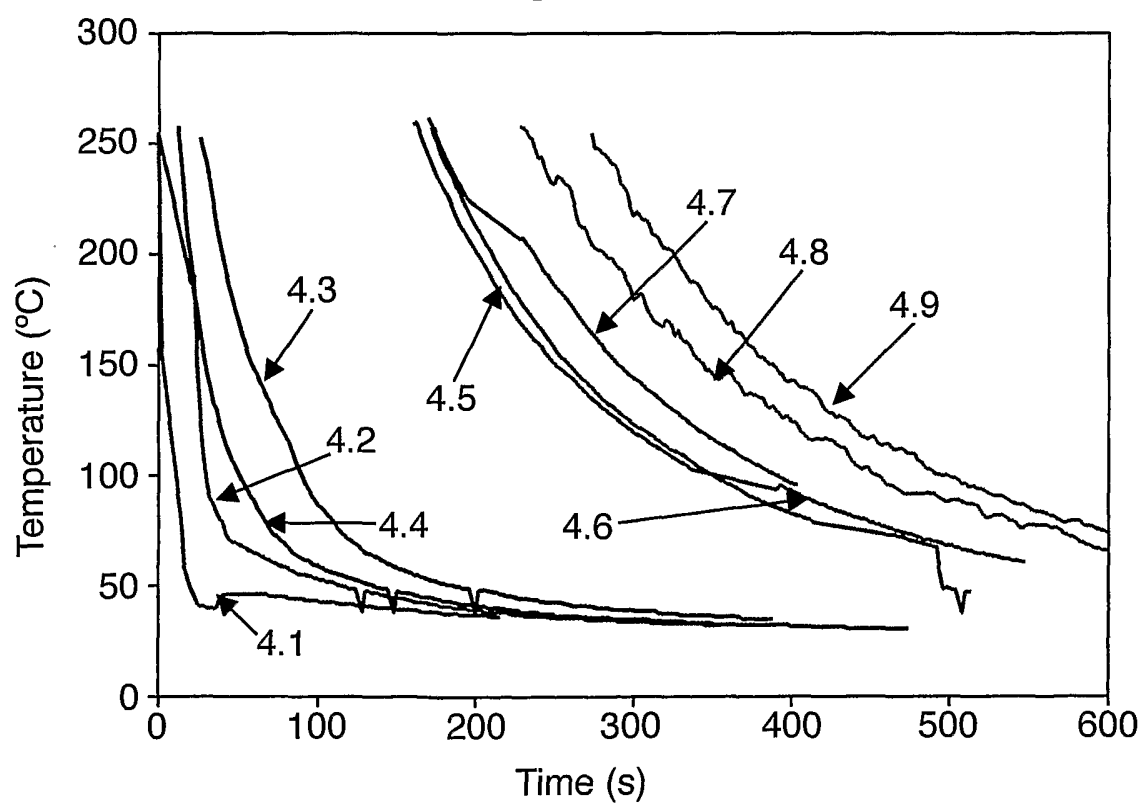


Fig.4.

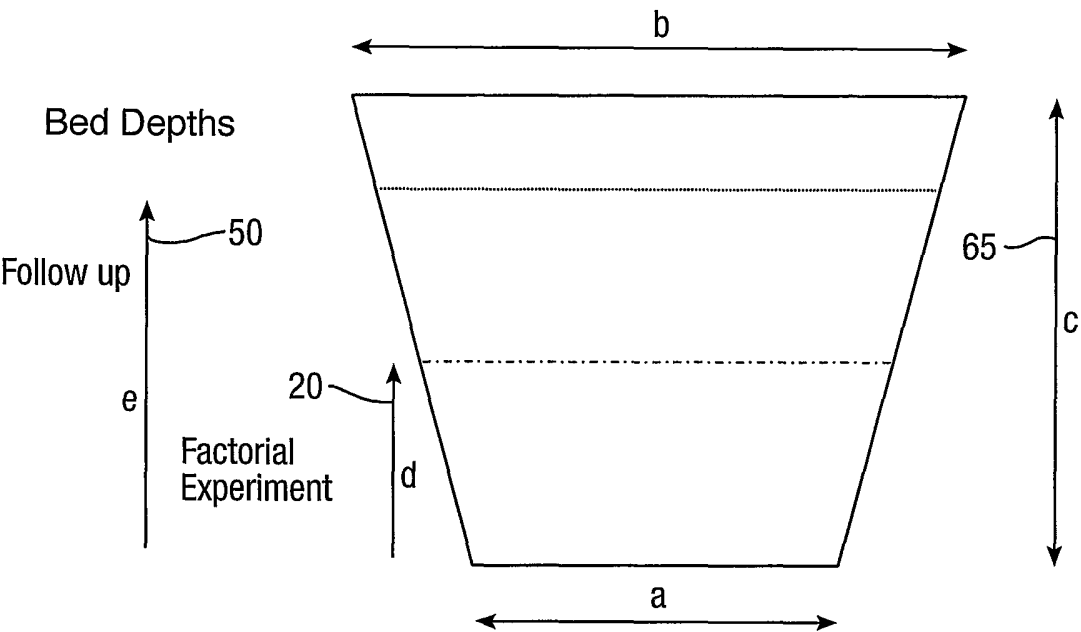
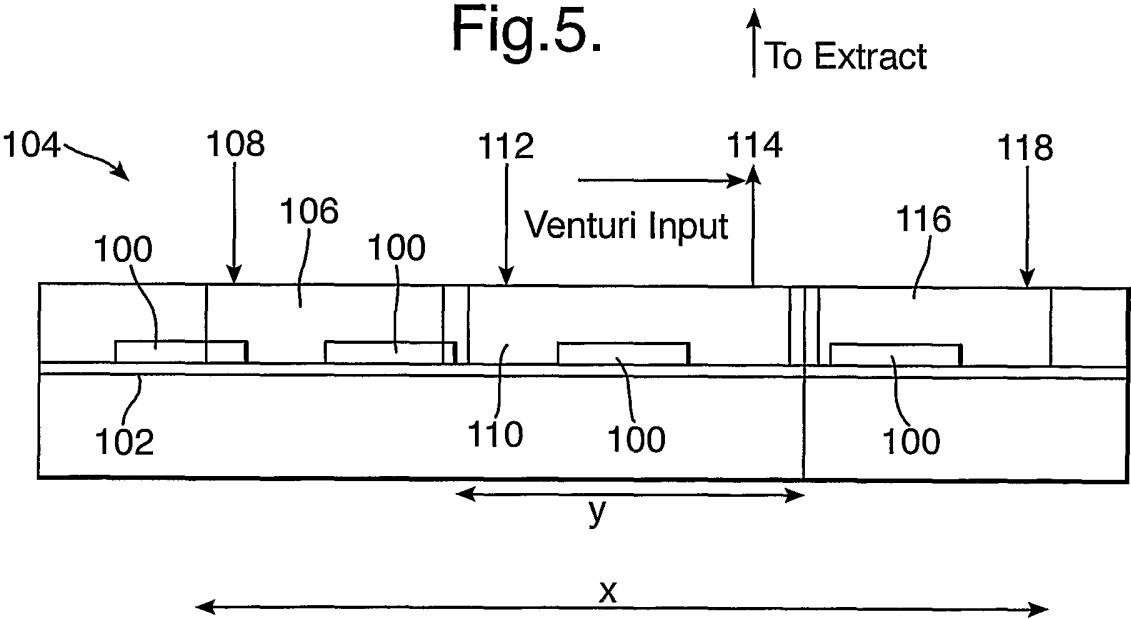
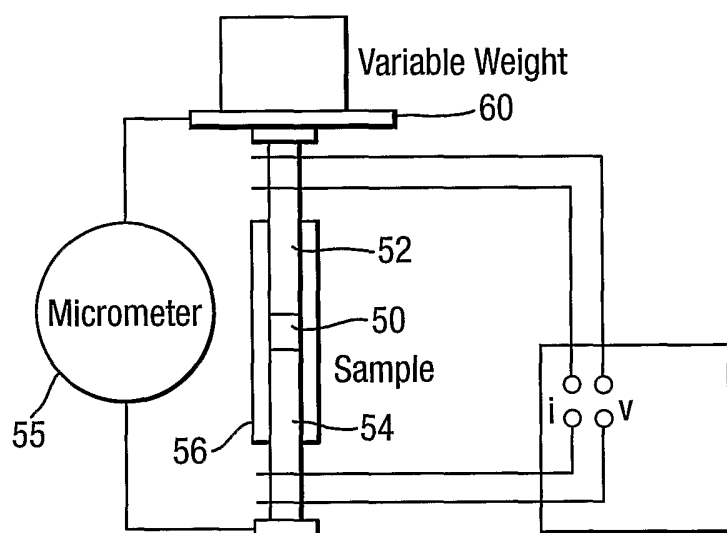


Fig.5.



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Fig.6.



INTERNATIONAL SEARCH REPORT

Interr il Application No
PCT/GB2005/002063

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

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 C01B C09C

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 4 859 499 A (SAUVINET ET AL) 22 August 1989 (1989-08-22) column 2, lines 34-56 column 4, lines 26-48 example IV	1, 2, 5-8, 12
X	US 6 533 966 B1 (NONNINGER RALPH ET AL) 18 March 2003 (2003-03-18)	15-17
A	column 4, line 64 - column 5, line 42 column 7, lines 30-67 column 12, lines 27-43 example 1b)	1-14
A	US 5 744 118 A (IMAMURA ET AL) 28 April 1998 (1998-04-28) column 11, lines 28-67 examples 3-5	1-17
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☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

12 August 2005

Date of mailing of the international search report

23/08/2005

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 03/095360 A (W. C. HERAEUS GMBH & CO. KG; SEROLE, BERNARD; SEROLE, MICHELLE) 20 November 2003 (2003-11-20) the whole document -----	1-11
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INTERNATIONAL SEARCH REPORT

Information on patent family members

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