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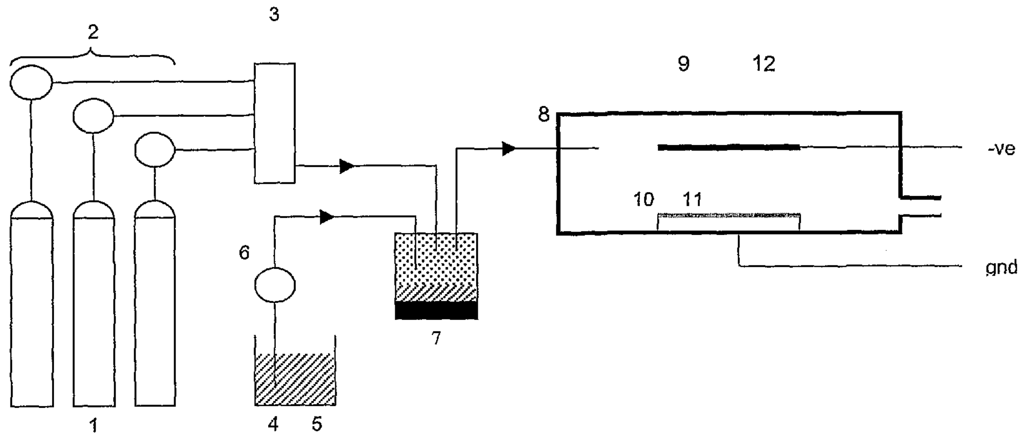
(54) Title: IMPROVED DEPOSITION PROCESS



(57) Abstract: A deposition process which is suitably for depositing metal oxide thin films, such as films of transparent conducting oxides, onto a substrate, comprises feeding a decomposable metal-polymer composition (5) to a nebuliser (7) with a carrier gas, to form an aerosol. The aerosol is contacted with a substrate (11), which is heated to or above the decomposition temperature of the polymer, causing metal oxide to be deposited on the substrate.

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IMPROVED DEPOSITION PROCESS

The present invention concerns an improved deposition process especially suitable for the deposition of films of metal oxides onto substrates. The process may produce thin films or thick films, as understood by the electronics engineer.

It is known to deposit thin films of metal oxides by vacuum deposition sputtering in forming microelectronics parts, and for depositing infra-red reflective layers on glass. Although such vacuum deposition processes have been developed to be efficient, they remain very expensive in terms of equipment and operating costs.

It is also known from US 5,278,138 to use aerosol-based processes for the deposition of multicomponent metal oxides by forming an aerosol of a solvent component with metal oxide precursor compounds or complexes. The solvent is non-reactive towards the precursor compounds or complexes and the substrate, and the precursor compounds or complexes are substances such as yttrium tetramethylheptanedionate or copper acetate.

There remains a need for a relatively simple and inexpensive method for depositing thin films of metal oxides, especially for conducting metal oxides (technically these are semi-conducting) and more especially for transparent conducting metal oxides.

The present invention provides a method for depositing thin films of metal compounds, especially metal oxides, onto a substrate, comprising depositing onto a substrate maintained at an elevated temperature, an aerosol comprising a precursor metal-polymer composition wherein the metal forms the desired metal compound and is bound in the composition to a polymer which decomposes at a temperature at or below said elevated temperature, in a carrier gas, such that upon contact of the aerosol droplets with the substrate, the polymer is decomposed to deposit metal on the substrate and simultaneously or subsequent to deposition of the metal on the substrate, the metal is converted into the desired metal compound, especially it is oxidised to the desired metal oxide. The method of the invention does not require vaporisation of the precursor metal-polymer composition and desirably the decomposition temperature of the precursor metal-polymer composition is desirably below its normal vaporisation temperature.

The invention further provides a precursor metal-polymer composition comprising a metal bound to a polymer which composition decomposes at an elevated temperature and permits the deposition of the metal onto a substrate. The polymer desirably has a sharp onset of decomposition, and desirably decomposes to form only gaseous products such as carbon dioxide. Acrylate-based polymers, including co-polymers, presently offer the best opportunities, but the invention is not to be considered as being limited thereto.

The precursor composition may be in the form of a bulk precursor liquid or in the form of an aerosol. Solvents or carriers, including water and low-boiling organic solvents may be incorporated in the composition. Suitable solvents or carriers are those that can readily be nebulised, and include methanol, ethanol, IPA and toluene.

The metal may be selected from the group consisting of, but not limited to, nickel, copper, zinc, cobalt, chromium, aluminium, indium, gallium, tin, lithium, calcium, scandium, strontium and germanium. Although it is presently preferred to use just a single metal in the process and in the precursor compositions, it is envisaged that mixtures of different metal precursors may be used, and further that the deposited metal oxide film may be doped with minor quantities of metals or metal oxides. It is envisaged that the invention may be applied to high electronegativity, high valency metal ions such as tungsten or vanadium.

The polymer preferably has a thermal decomposition profile, as evidenced by thermal analysis, that is very rapid at specific temperatures and results in complete burn-off with no carbon residue. Polymers and co-polymers of acrylate monomers are expected to be particularly suitable polymers for use in the present invention.

The loading of metal ions to coordinating monomer units may vary widely. High metal loadings can, however, lead to cross-linking, with consequential formation of high molecular weight materials which tend to precipitate from the aerosol composition prior to formation of the aerosol. Low molecular weight polymers, for example of MW 100 to

10,000, are generally preferred because of the advantage of low solution viscosity, as required for nebulisation, and a possible high metal content.

A suitable polymer may be prepared by adding methacrylic acid monomer to acetone or to water, with stirring. Aqueous hydrogen peroxide is added to initiate free radical polymerisation. The mixture is stirred for approximately 72 hours, and residual solvent is removed by rotary evaporation to give, depending upon processing conditions, a viscous liquid, a waxy solid or a dry powder. Copolymerisation may be achieved by adding other monomers such as styrene or methylmethacrylate to the monomer solution before the hydrogen peroxide addition. The polymer, eg poly(methacrylic acid) is dissolved in water then partially or completely neutralised by the addition of ammonia solution. This yields the polymer backbone with acetate groups along the chain. The addition of a solution of an appropriate salt produces an insoluble material which precipitates then redissolves slowly. Excessive amounts of metal salt result in an insoluble material which is assumed to arise from cross-linking of polymer chains through coordination of the metal ions.

The metal may be reacted with a monomer prior to polymerisation or copolymerisation. For example, metals that form basic hydroxides may be reacted as hydroxides with monomers having acid groups. Thus, methacrylic acid is diluted to approximately 50:50 solution with acetone and an excess of metal hydroxide, for example $Cu(OH)_2$, is added and the mixture stirred for 30 minutes. The solid is separated from the supernatent by filtration or centrifugation and discarded. The supernatent is treated by thermal or rotary evaporation in order to remove the remaining solvent, to yield a metal-monomer.

In the case of metal oxides which are weakly basic, such as $Ni(OH)_2$, these do not react with methacrylic acid. In such a case, the methacrylic acid may be neutralised using ammonia solution, and the appropriate metal salt solution is added in a stoichiometric amount. The product may be separated and purified using filtration (to remove precipitated precursor) or by treatment with cold acetone to remove ammonium salts.

The metal-polymer precursor may then be formed using conventional polymerisation techniques, for example using methacrylic acid or another monomer.

Substrates suitable for use in the invention are those capable of surviving the treatment conditions and are generally of monolithic physical form, preferably flat in form. Various types of glass, including but not limited to AF45 and 1737F (commercially-available types of sodium-free glass), and wafers of other materials such as silicon, sapphire, plastics that have adequate thermal and chemical stability under the processing conditions and quartz, are preferred.

The aerosol is dispersed in a carrier gas compatible with the substrate and the aerosol droplets themselves, and accordingly for the formation of oxide layers, an inert gas in combination with a minor amount of oxygen or air is preferred. Compressed air itself, approximately 75% N_2 and 25% O_2, is generally a suitable carrier gas.

The method of the invention is suitably carried out by contacting the aerosol with a substrate which is heated to a temperature above the decomposition temperature of the metal-polymer precursor, by feeding the aerosol in the carrier gas over the heated substrate. The substrate temperature is suitably the specific decomposition temperature of the polymer being used. The oxygen in the carrier gas causes formation of the desired oxide *in situ*. The method may include post treatments under one or more atmospheres different from the carrier gas, such as annealing at a temperature in the range 300 to 600 °C, and a variety of atmospheres, such as nitrogen, oxygen, reduced pressure, may be used to achieve a desired phase of the oxide metal coating or other variation of the deposited film coating.

The deposition is desirably assisted by electrostatic attraction of the aerosol droplets onto the substrate. A technique that may also assist deposition, especially if there are significant boundary layer effects, is ultrasonic disruption of the boundary layer or another mechanism of disrupting the boundary layer such as turbulence.

The invention may be modified to produce thin film coatings other than metal oxides, by the use of different metal precursors in combination with the polymer, and different carrier gases. Thus it is possible to conceive of a process using an aerosol comprising a metal-polymer precursor and ammonium thiocyanate using a carrier gas comprising hydrogen sulphide, to produce a metal sulphide thin film coating. Similarly, metal nitride coatings may be produced.

Whilst the initial purpose of the invention is to deposit thin film metal oxides which are transparent and conducting, the invention is contemplated as being suitable for the production of coatings which are reflective or transparent in part of the visible spectrum (such as coatings on window or windscreen glass), or which affect the colour of the substrate, or which improve certain surface properties such as wear or scratch resistance, or the deposition of a photoactive self-cleaning coating on window glass. Additionally, the deposited layer may form part of a multilayer structure, including acting as a barrier layer in such a structure, such as a thermal barrier.

It is expected that at least the preferred embodiments of the present invention will demonstrate the following advantages:

Because the oxide is formed only at the surface, and no oxide particles are required to be formed and deposited, the metal oxide film is of high quality;

The metal-polymer precursor is chemically stable and robust, being resistant to changes caused by solvent evaporation during mass transport;

Mixed or doped oxides may readily be prepared by using the same polymer system with appropriate ratios of metal ions;

The production method requires low capital expenditure on equipment and low operating costs; and

The coatings produced are comparable, in terms of conductivity at least, to coatings produced by vacuum deposition methods.

The inventors consider that the invention may be used to produce:

High dielectric constant materials for DRAM chips, particularly TaO_x;

Plasma display dielectric materials requiring large area deposition, particularly MgO;

Spintronic materials, ZnO: Mn, TiO_2: Co, SnO_2: Mn. Oxide-based diluted magnetic semiconductors;

Thermochromic and electrochromic layers such as VO_2 and WO_3 and heterostructure thereof;

Transparent electronics, transparent diodes and transistors utilizing n-p and n-p-n junctions;

Gas sensors, oxygen detection with semiconducting thin films. Bulk conductance types TiO_2 (doped with Nb, Cr in some instances), $SrTiO_2$, Ga_2O_3, CeO_2, $BaTiO_3$ (poss. Nb doped) and surface conductance types SnO_2 (plus dopants Li, Pt etc.), ZnO (plus dopants) Cu_2O and Nb_2O_5.

The invention is more particularly described by reference to the accompanying schematic diagram, which is intended to be illustrative and not limiting.

Referring to the diagram, gas cylinders (1), supplying different gases in predetermined quantities through regulators (2) feed into a gas mixer and pressure let-down device (3) to form an oxygen-containing carrier gas. A vessel (4) contains metal-polymer precursor solution indicated by (5) which solution is fed by a pump (6) (or gravity-fed) into a commercial ultrasonic nebuliser (7). The mixed gases are also fed at approximately atmospheric pressure into nebuliser 7, and a tube (8) is connected from the nebuliser 7 into a treatment chamber (9). In a variant, not all the gases are fed into the nebuliser, and either a proportion of the mixed gases, or one component of the gases, is added subsequently to the aerosol. An aerosol of metal-polymer precursor solution travels from the nebuliser 7 into treatment chamber 9. The treatment chamber 9 contains a heating plate (10) which is electrically grounded. The heating plate carries a substrate sample (11) which is heated to the appropriate polymer decomposition temperature by the hotplate. A metal grid (12) mounted in the treatment chamber is held at a negative potential (of 5 kV), and assists aerosol droplets of metal-polymer precursor solution to deposit on the substrate.

Using a nickel poly(methacrylate) solution in water, and a compressed air carrier gas, a coating of nickel oxide of 20-30 nm thickness was formed on a 1737F glass substrate. Initial measurements show a resistance for the film of 10Ωcm.

Using an analogous process, a NiO p-type film has been deposited.

CLAIMS

1. A method for depositing thin films of metal compounds, especially metal oxides, onto a substrate, comprising depositing onto a substrate maintained at an elevated temperature, an aerosol comprising a precursor metal-polymer composition wherein the metal forms the desired metal compound and is bound in the composition to a polymer which decomposes at a temperature at or below said elevated temperature, in a carrier gas, such that upon contact of the aerosol droplets with the substrate, the polymer is decomposed to deposit metal on the substrate and simultaneously or subsequent to deposition of the metal on the substrate, the metal is converted into the desired metal compound, especially it is oxidised to the desired metal oxide.

2. A method according to claim 1, wherein the precursor metal-polymer composition comprises a solvent or carrier capable of being nebulised and which is decomposed or evaporated at the decomposition temperature of the polymer.

3. A method according to claim 1 or 2, wherein the polymer is an acrylate-based polymer or co-polymer.

4. A method according to any of the preceding claims, wherein the polymer has a molecular weight of from100 to 10,000.

5. A method according to any one of the preceding claims, wherein the aerosol is carried in an oxygen-containing gas.

6. A method according to claim 5, wherein the oxygen-containing gas is air.

7. A method according to any one of the preceding claims, wherein the deposition of aerosol droplets is assisted by electrostatic attraction.

8. A method according to any one of the preceding claims, used to produce a transparent conducting oxide.

9. A method according to any one of the preceding claims, wherein the substrate is a glass or a wafer of silicon, sapphire, plastics that have adequate thermal and chemical stability under the processing conditions, and quartz.

10. A method according to any one of the preceding claims, comprising an additional step of a post treatment under one or more atmospheres different from the carrier gas, such as annealing.

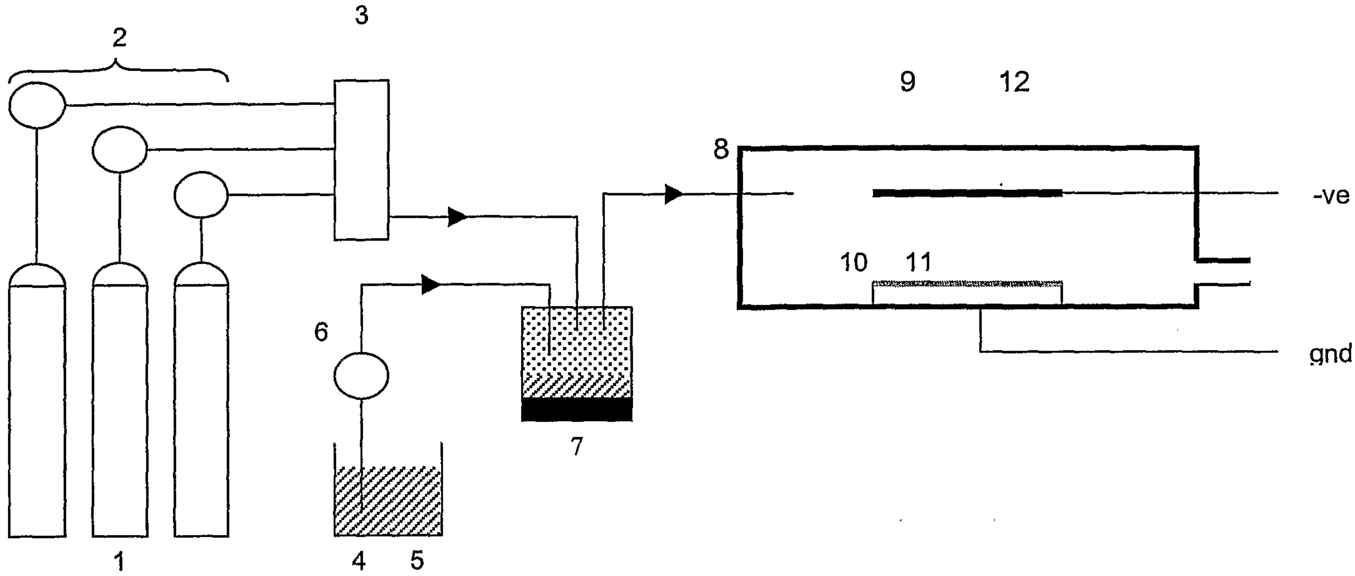
11. A method according to claim 1, substantially as hereinbefore described.

12. A precursor metal-polymer composition comprising a metal bound to a polymer, which polymer decomposes at an elevated temperature and permits the deposition of the metal onto a substrate.

13. A precursor composition according to claim 12, comprising also a solvent or carrier which permits nebulisation.

14. A precursor composition according to claim 12 or 13, in the form of an aerosol.

15. A precursor composition according to claim 12, substantially as hereinbefore described.



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A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C23C16/18 C23C16/40

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 C23C

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

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, PAJ, WPI Data, INSPEC, COMPENDEX

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	claims 1,2,7,8,11-16; examples 1,4,5	7
X	US 2003/134511 A1 (KIM YOUNSOO) 17 July 2003 (2003-07-17) paragraph ‘0030! - paragraph ‘0039!; claims 1-6	1,2,9, 11,12, 14,15
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[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
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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

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X	JIA Q X ET AL: "Polymer-assisted deposition of metal-oxide films" NATURE MATERIALS NATURE PUBLISHING GROUP UK, ‘Online! vol. 3, no. 8, August 2004 (2004-08), pages 529-532, XP002347561 ISSN: 1476-1122 Retrieved from the Internet: URL:http://www.nature.com/nmat/journal/v3/n8/pdf/nmat1163.pdf> ‘retrieved on 2005-10-03!	12,13,15
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