

Design of Bi-Metallic Precursors for Synthesis of Thin Inorganic Metal Oxide Films by Sol Gel Route

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ABSTRACT

Recently gallium and indium alkoxides are being used as precursors and their applications as gas sensors, amorphous oxide semiconductors within thin film transistor (TFT) technology, as photoelectric coatings and as transparent conducting coatings. These alkoxides also act as excellent precursors to their oxides via decomposition processes, at relatively low temperature, using chemical vapour deposition (CVD) to form thin films. At the same time the synthesis and characterization of nanoparticles display many unique properties like electrical, optical, and magnetic, somewhat different to the bulk system and interesting applications in biology, catalysis, sensors, mechanics and electronics fields. The mixed-oxides were obtained and characterized by a high dispersion of the active phase in the matrix on both molecular and nanometer scale. The versatility of the sol-gel route makes possible to obtain the final material as powders, bulk and coating films. The different metal oxide films were grown using a variety of precursors. The films deposited were not oxygen deficient and little carbon contamination was observed. Thin films of indium gallium oxide, and zinc gallium oxide were also produced.

Keywords : Gallium, Indium, Alkoxides, Precursor, TFT, CVD, sol-Gel Route, Nano Particles.

I. INTRODUCTION

In the recent years there has been increasing interest in gallium and indium alkoxides for use as precursors to group 13 oxide thin films. These materials find applications as gas sensors, amorphous oxide semiconductors within thin film transistor (TFT) technology, as photoelectric coatings and as transparent conducting coatings. Gallium and indium alkoxides have been shown to act as excellent precursors to their oxides via decomposition processes, at relatively low temperature, using chemical vapour deposition (CVD) to form thin films. At the same time work is also going on the synthesis and characterization of nanoparticles because of their small size and high surface area and display many unique properties like electrical¹, optical², and magnetic^{3, 4}, somewhat different to the bulk system.

Nanoparticles exhibit interesting applications in biology, catalysis, sensors, mechanics and electronics fields⁵⁻⁷. If nano-scaled particles are dispersed in a host matrix, a new nanocomposite material will be formed that possesses some unique properties both of the nanoparticles and the matrix. The sol-gel synthesis of inorganic nanocomposites based on highly dispersed and nanosized active phases that exhibit catalytic, electro-optic, ferroelectric, and non-linear optical properties. The special attention was given to the thin films preparation, fundamental for the realization of electronic devices. Compared with the conventional ceramic routes, such as co-precipitation, grafting, impregnation, the sol-gel exhibits many advantages, among them the low process temperature, the high control of purity, composition, microstructure and textural properties of the final material.⁸⁻¹⁰ This synthetic procedure allows for mixed-oxides to obtain

materials characterized by a high dispersion of the active phase in the matrix on both molecular and nanometer scale.¹¹⁻¹⁶ Moreover, the versatility of the sol-gel route makes possible to obtain the final material as powders, bulk and coating films. For films fabrication, in comparison with the conventional deposition techniques, such as chemical vapor deposition, sputtering and pulsed laser deposition, the sol-gel offers a better control of the chemical composition, excellent homogeneity, low process temperature, uniformity over large area allowing to produce high-quality films up to micron thickness.^{8,17} Special emphasis is attributed to the influence of the process parameters on the control of the dispersion degree of the active phase.

II. STUDY OF SOL-GEL

The most preferred precursors are alkoxides with general formula: $M_x(OR)_y$ where M = element with valence y; R = alkoxide group. The role of alkoxides is to control the chemical synthesis of oxides in the following way:-

1. Easy to purify, a lot of alkoxides can be distilled in order to obtain highly pure products;
2. Wide variety, it is possible to choose R among a large number of alkyl groups in order to obtain the required reactivity;
3. Possible control, of the alkoxides hydrolysis and the polycondensation of hydrolysed species;
4. Mixed alkoxides, as a further control means of the stoichiometry and homogeneity of the final products.
5. Gelation, hydrolysis and polycondensation.

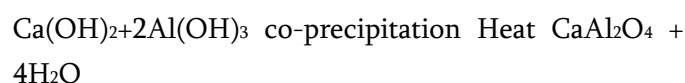
The transition from sol to gel involves two key steps, hydrolysis and polycondensation reactions. The hydrolysis takes place by small amounts of water. Since water and alkoxides are immiscible, a mutual solvent such as alcohol, is normally used as a homogenizing agent. In the hydrolysis reaction, the

alkoxide groups (OR) are replaced stepwise by hydroxyl groups (OH). The hydrolysis rate depends on many factors. Indeed, the reaction can be favourably promoted by an increase in the charge density on the metal, the number of metal ions bridged by a hydroxo- or oxo-ligand, and the size of the alkyl groups.^{18,19}

III. STUDY OF SOL-GEL PRECURSORS

High surface area nanocrystalline metal oxides of magnesium, calcium, aluminium, and transition metals have been used as adsorbents and catalysts.²⁰⁻²⁵ Core/shell bimetallic mixtures, such as MgO coated with V_2O_3 , possess their own unique sorption and catalytic properties.²⁶ Furthermore, mixed oxides of the type MAl_2O_4 (M=Ca, Mg, Mn, Co, Fe, Ni, Zn) have found uses in many important processes, such as Fischer-Tropsch catalysts or as precursors to new ceramics.^{27,28} Generally, these oxides of the MAl_2O_4 type have been synthesized by three methods:-

- (i) Co-precipitation of metal hydroxides followed by heat treatment at high temperatures, as for $CaAl_2O_4$, for example:



This method was affected by partial segregation to CaO and Al_2O_3 individual solid oxides as final products (phase segregation).

- (ii) Physical mixing of hydroxides, oxides, alkoxides, or nitrates followed by high temperature treatment. This method was also complicated by the tendency toward phase segregation.

Hydrolysis of bimetallic bridged alkoxides, such as $M[Al(OR)_4]_2$, shown below.²⁹⁻³⁰ In theory, if hydrolysis of all OR groups ($OR \rightarrow OH$) were to occur at the same rate, then a homogeneous hydroxide (and after dehydration, a homogeneous oxide) could be obtained.

However, the doubly bridged Al-O(R)-Al groups, due to the presence of two Al cations, would probably be hydrolyzed faster than the terminal RO-Al groups, thus the bridge would be cleaved and segregation of phases would occur.

Due to above existing problems in all these synthetic methods, a new method was developed, where the M-O-Al bridges in the pure molecular precursor are not cleaved upon hydrolysis. Therefore, we have prepared new bimetallic m-oxo molecular precursors of the form (RO)_xAl-O-M-O-Al(OR)_y as the M-O-Al bridging oxo group was much less sensitive to hydrolysis compared to the M-O(R)-Al group and, therefore, a homogenous phase could be maintained throughout hydrolysis and subsequent dehydration. Besides this, a modified aerogel was synthesized to get high surface area nanocrystalline MA₂O₄. It made controlled stoichiometric hydrolysis of the bimetallic m-oxoalkoxide in an alcohol-toluene solvent mixture to produce a high quality gel, which was placed in an autoclave and heated to near supercritical conditions (300 °C) and the solvent quickly vented and removed, so that high surface area hydroxides were formed and were dehydrated under vacuum conditions, leading to high surface area nanocrystalline MA₂O₄ oxide as a homogeneous phase.

In the preparation of homogeneous phase bimetallic oxides, Zircon, ZrSiO₄, is the only crystalline phase in the binary SiO₂-ZrO₂ system that is stable under 1676 °C. This oxide exhibits low thermal expansion, low thermal conductivity, and high resistance to thermal shock. To take advantage of such properties, which are very interesting for high temperature applications, the zircon should be highly pure. Indeed, impurities such as Al₂O₃, Fe₂O₃, TiO₂ and SiO₂, found in natural zircon sand, can lead to a lowering of its decomposition temperature and alteration of its mechanical properties. Although difficult, the preparation of high-purity ZrSiO₄ has already been the subject of a great number of research papers. Various different synthetic routes have been

investigated. The formation of zircon powders at temperatures as low as 150 °C is possible under hydrothermal conditions.³¹⁻³³ Sol-gel processing has also been used by combining numerous precursors in aqueous or organic media, including sols, salts and alkoxides.³⁴⁻⁴⁸ In this case, literature data indicate that pure zircon is produced at high temperatures varying between 1100-1500 °C according to the procedure followed. However, Mosset et al.³² have shown that partially crystallized zircon can be formed at 100 °C. The work discusses zircon synthesis by a new aqueous semi-alkoxide route, combining tetraethoxysilane (TEOS) with zirconyl nitrate ZrO(NO₃)₂.xH₂O: an aqueous solution of zirconyl nitrate in which TEOS has been hydrolysed into silicic acid constitutes a homogeneous zircon precursor. A procedure for the preparation of spherical ZrSiO₄ particles from the starting precursor solution is also mentioned in literature which is used for obtaining pure zircon powders with controlled morphology. Titanium dioxide nanostructures have been widely investigated as materials for solar cells,⁴⁹ photocatalysis,⁵⁰⁻⁵¹ optoelectronic devices,⁵² photoelectrochromic windows,⁵³ and sensors.⁵⁴ For these applications, the forms of titania—their crystal size, shape, and structure are critically important to their performance. The simplest and most commonly reported synthetic procedure for preparing TiO₂ nanostructures is the sol-gel method in which titanium alkoxide or titanium chloride precursors are hydrolyzed in an aqueous solution. Nanoparticles,⁵⁵ nanowires,⁵⁶⁻⁵⁷ nanotubes,⁵⁸⁻⁵⁹ and ordered 2- and 3-dimensional porous films⁶⁰ are just some of the architectures available to researchers via sol-gel chemistry. Despite the research advances in this area, it is still challenging to predict the crystal size and structure from a particular synthetic protocol. Furthermore, the reproducible synthesis of small-batch TiO₂ nanocrystals remains a challenge. The synthetic knowledge to vary systematically the morphological and electronic properties of nanostructured systems in a reproducible way is important for advancing both fundamental and applied research. This is especially

true for TiO₂ nanoparticles used in the fabrication of mesoporous films for dye-sensitized solar cells (DSSCs; Grätzel cells),⁶¹⁻⁶² one of the promising unconventional future technologies of interest to the solar cell community. For instance, varying the particle shape can affect the particle packing density, which, in turn, can alter light harvesting⁶³ and electron transport in TiO₂ films.⁶⁴ Variation in the particle density (porosity) changes the average coordination number of particles in films, the consequence of which alters the electron transport pathway and, therefore, the electron dynamics.⁶³

Volatile organometallic oxide precursors offer several advantages for the synthesis of nano-scaled metal oxides in different environments because they can be used in chemical-vapour-synthesis (CVS), in solution (non-hydrolytic and hydrolytic sol-gel-synthesis) or in solid state synthesis (synthesis of nanoscaled solids).⁶⁵ We are currently using organozinc-alkoxide⁶⁶ and -siloxide clusters⁶⁷ as molecular models and volatile multiple precursors for nanoscaled ZnO, Zn and ortho-zinc silicate (Zn₂SiO₄) particles.⁶⁸ ZnO is one of the most important substrates in heterogeneous catalysis⁶⁹ but its (micro)-structure-reactivity relationship is not yet well understood even after more than 30 years of intensive research. We have shown that organozinc siloxide clusters⁶⁷ can be used as remarkable versatile precursors for the synthesis of highly active nanocrystalline ZnO and heterometal ZnO supports for the conversion of CO₂ and H₂ into methanol and H₂O.⁶⁹ Remarkably, alkali metal ion-modified ZnO supports show uncommonly strong one- and two-electron donor properties and are unusual super basic heterogeneous catalysts.⁷⁰ Since the catalytic activity of ZnO supports can be drastically enhanced in the presence of several promoter components (e.g., Cu particles, alkali metal ions, etc.) it is furthermore highly desirable to gain access to appropriate single-source precursors for such multi-component ZnO substrates which are far less developed. Therefore we are also currently focusing on the synthesis of structurally defined heterometal

zinc-alkoxide and-siloxide clusters as molecular single-source precursors for alkali metal-modified ZnO systems. We learned that the structural chemistry of seemingly simple mixed alkali metal and zinc alkoxides is only scarcely developed, although they have a long tradition as reactive species in both organic and inorganic synthesis. For example, it is well known that dialkylzinc compounds can be highly activated as alkyl transfer reagents towards unsaturated organic substrates in the presence of alkali metal alkoxides,⁷¹ and diorganozinc compounds react with CO to give acyls but only in the presence of alkali metal alkoxides as promoters.⁷²

IV. RESULT AND DISCUSSION

The different metal oxide films were grown using a variety of precursors. The films deposited were not oxygen deficient and little carbon contamination was observed, which is attributed to being a direct result of precursor design. Thin films of indium gallium oxide, and zinc gallium oxide were also produced from the *in situ* reactions of InMe₃, GaMe₃ and HOCH₂CH₂OMe (for Ga_xIn_{2-x}O₃) and ZnEt₂, GaMe₃ and HOCH₂CH₂OMe (for Ga_xZn_yO) on silica substrates.

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