



Review

Molecular precursor approach to metal oxide and pnictide thin films



Peter Marchand, Claire J. Carmalt*

Department of Chemistry, University College London, Christopher Ingold Laboratories, 20 Gordon St., London WC1H 0AJ, UK

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ARTICLE INFO

Article history:

Received 30 November 2012

Received in revised form 24 January 2013

Accepted 24 January 2013

Available online 18 February 2013

Keywords:

Gallium oxide

Indium oxide

Single-source precursors

Bismuth oxide

Titanium nitride

Tungsten nitride

Titanium phosphide

Titanium arsenide

Zirconium carbonitride

Chemical vapour deposition

ABSTRACT

Molecular precursors for the preparation of main group metal oxide and transition metal pnictide thin films have been developed. This work involves the design and synthesis of single-source precursors that contain all the elements required in the thin film. Design of the ideal precursor presents a significant challenge since they must be volatile, non-toxic and thermally stable. Therefore the precursors have been tailored to give clean, reproducible decomposition leading to high quality thin films with good coverage of the substrate. In this review key aspects of precursor synthesis and thin film deposition developed in our group are described. The range of precursors developed for main group oxides, in particular gallium and indium oxide, are discussed, with the most studied being the donor-functionalized alkoxides of the type $[R_2M(OR')]_2$ ($M = Ga, In$; $R = H, Me, Et$; $R' = CH_2CH_2NMe_2, CH_2CH_2OMe$ etc.). Preliminary mechanistic studies suggest that monomers are formed in the gas phase via stabilization of the metal centre by the donor atom (N or O). Precursors to transition metal pnictides have also been developed, including guanidates, imides, phosphine and arsine compounds and an overview of their use in film deposition is given.

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1. Introduction

The most common approach for the chemical vapour deposition (CVD) of many materials, such as oxides, nitrides, phosphides and arsenides, is to use two or more separate precursors that react individually on the growing film [1]. This procedure, however, makes it difficult to control film stoichiometry and usually high

* Corresponding author. Tel.: +44 2076797528.

E-mail address: cj.carmalt@ucl.ac.uk (C.J. Carmalt).

deposition temperatures are required. In addition, in some cases, toxic or pyrophoric materials are utilized in the production of the films. Another approach to such materials is to use a single-source precursor, which consists of the elements (M–E) in the material (e.g. M = Ga and E = O for Ga₂O₃) bonded at the core of the molecule, with various other ligands attached to each of the elements [2]. The reaction pathway involves adsorption of the precursor without breaking the M–E bond but with loss of the ancillary ligands, affording a thin film of the desired material. The advantages of the single-source precursor approach are fourfold. First, the stoichiometry of the precursor can be retained in the film. Second, the high deposition temperatures often associated with multi-source depositions are generally lowered. Third, the precursor delivery system can be simplified. Fourth, better homogeneity is possible since the desired elements are effectively premixed at the molecular level. Thus, single-source precursors can provide a simple and clean route to films, eliminating the need for a mixture of precursors which can often be toxic and/or expensive, as well as involving complicated gas-phase reaction dynamics which can result in the formation of non-stoichiometric films [2,3].

Despite the numerous advantages outlined above, there are disadvantages to using single-source precursors, for example, such precursors often have low vapour pressures, contamination of the films can result from the decomposition of the ligand and the stoichiometry of the precursor is not always retained in the film. However, advances in variants of deposition techniques, such as CVD, have gone some way to overcome many of these issues. For example, aerosol-assisted (AA)CVD, a variant of conventional CVD processes, addresses the delivery and availability problems associated with single-source precursors [4,5]. AACVD uses a liquid–gas aerosol to transport soluble precursors to a heated substrate and is a useful method when a conventional atmospheric or low pressure CVD precursor proves involatile or thermally unstable. Compared to conventional CVD, the AACVD method uses aerosol droplets to transport precursors, with the aid of inert carrier gases. Therefore, in AACVD volatility is no longer crucial and this allows for a wider choice of precursors being available for use and can lead to high quality films at low cost. AACVD can also result in high deposition rates due to the possibility of high mass-transport rate of the precursor, as well as simplification of the delivery. By designing precursors specifically for AACVD, the restrictions of volatility and thermal stability are lifted, and new precursors and films can be investigated. Furthermore, different and unique morphologies of films can be obtained by AACVD due to the influence of the solvent on the deposition, which could potentially lead to improved properties.

Our main efforts have concentrated on the preparation of precursors and their subsequent deposition to thin films of metal oxides and nitrides although this has been extended to other materials. Recent research has concentrated on the synthesis of precursors for the production of gallium and indium oxide thin films using AACVD, as well as combinatorial AACVD (cAACVD). A variety of methods to deposit these films exists, as do a large selection of well-defined molecular compounds which contain a preformed M–O bond (M = Ga, In) that can be used in deposition processes without an additional oxygen input, i.e. single-source precursors. However, we have developed a range of precursors for main group oxides, with the most studied being the donor-functionalized alkoxides, of the type [R₂M(OR')]₂ (M = Ga, In; R = H, Me, Et; R' = CH₂CH₂NMe₂, CH₂CH₂OMe etc.). These ligands were chosen for AACVD as they lead to precursors which are less air/moisture sensitive and have increased solubility. The high moisture sensitivity of many main group alkoxides makes them difficult to use in solution-based CVD [6]. Therefore, modified alkoxides, such as the donor functionalized ligands, which have an increased coordinative saturation at the metal centre, provide

more stability and also eliminate the necessity of introducing an extra donor group to stabilize the electron deficient main group alkoxide complex. Moreover, preliminary mechanistic studies using gas phase electron diffraction indicates that monomers are formed in the gas phase via stabilization of the metal centre by the donor atom. Other ligand types that we have investigated include β-ketonates, β-ketoimines and sesquialkoxides.

Another focus of our research has included precursors to transition metal pnictides – nitrides, phosphides and arsenides. The design, synthesis and use of transition metal guanidines, imido, phosphine and arsine compounds as precursors to metal pnictide or metal carbonitride thin films has been investigated and some of the compounds have been shown to be good precursors for use in low pressure CVD. This review provides an overview of the deposition of main group oxide and transition metal pnictide thin films using the molecular precursors developed in our group. The following abbreviations will be used: acac (acetylacetonate); ALD (atomic layer deposition); bdk (β-diketonate); CVD (chemical vapour deposition); EDXA (energy dispersive X-ray analysis); GED (gas-phase electron diffraction), hfac (1,1,1,5,5,5-hexafluoroacetylacetonate); ITO (tin-doped indium oxide); py (pyridine); TCO (transparent conducting oxide), TGA (thermogravimetric analysis); thd (2,2,6,6-tetramethylheptane-3,5-dione); TMEDA (*N,N,N',N'*-tetramethylethylenediamine); SEM (scanning electron microscopy), XRD (X-ray diffraction), XPS (X-ray photoelectron spectroscopy), WDX (wavelength dispersive X-ray analysis).

2. Precursors to gallium and indium oxide

Gallium oxide (Ga₂O₃) and indium oxide (In₂O₃) thin films are of interest due to their range of applications, which are related to their particular properties [7]. Since In₂O₃ films are conductive and transparent to visible light, they are used as a transparent conducting oxide (TCO), particularly when doped with other elements. For example, tin-doped indium oxide (ITO) thin films, with typical conductivities of (1–5) × 10³ S/cm and optical transparencies of 85–90%, are employed on a massive scale in numerous optoelectronic device applications [8,9]. Other elements have also been incorporated into indium oxide to increase its conductivity, including fluorine [10], sulfur [11] and gallium [12]. Gallium has also been used to dope zinc oxide, producing transparent conductive films as an alternative to ITO thin films for optoelectronic and electronic devices such as flat panel displays [13], solar cells [14] and light-emitting diodes [15,16].

Ga₂O₃ films, in contrast, are semiconducting above 500 °C and can act as a gas sensor for reducing gases, such as CO and ethanol [17,18]. However, when using gallium oxide films above 900 °C, the concentration of oxygen present in a system can be detected and so the function of the gas sensor could be switched from reducing gases to oxidizing gases [19,20]. Indium oxide films have also been shown to act as effective sensors, for example In₂O₃-modified gallium oxide thin films have been reported to be sensitive to ozone concentration and Ta-doped In₂O₃ showed a selective response to ethanol [21,22]. Furthermore, In₂O₃ nanorods have been reported to have sensing properties to formaldehyde [23].

Further applications include the use of gallium oxide films in zeolite catalytic systems [24], as white-light-emitting luminophores [25,26] and as solid electrolytes (for example doped-LaGaO₃) [27]. In addition, nitrogen-doped In₂O₃ thin films have been reported as visible light photocatalysts where on doping with nitrogen, the band gap of In₂O₃ was reduced from 3.5 eV to approximately 2.0 eV, thus electromagnetic radiation in the visible region can split water [28]. Zinc-doped gallium oxide has also been

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