

# MOCVD AND PRECURSOR DESIGN TO SYNTHESIS METAL OXIDE

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## ABSTRACT

*Applications of inorganic materials in the electronics industry have spurred activity in the area of chemical vapor deposition (CVD). This article discusses the increasingly sophisticated design strategies for precursor complexes through a series of case studies on CVD of metal oxide.*

## INTRODUCTION

The first step in CVD of any material is to consider which molecules may be useful as precursors. The factors that affect the choice of a particular source molecule for CVD of a specific material are complex and depend on the application under consideration. High-purity, dense metal films with controlled crystallite size and smooth surfaces deposited at relatively low temperature (< 500 °C), high deposition rate and low pressures are required for microelectronic application. Some of these constraints may be relaxed in other coating applications where, for example, high substrate temperatures can be tolerated or impurities are not detrimental.

CVD precursors can be broadly classified into three types: inorganic precursors, which do not contain carbon; metal-organic precursors, which contain organic ligands but no carbon-metal bond and organometallic precursors, which possess an organic ligand and a carbon-metal bond. There are a number of obvious precursor design requirements that have to be satisfied for a precursor to be useful for CVD. First of all the precursors need high vapor pressures, to achieve high transport rates. Inorganic precursors often exhibit low vapor pressures and high activation energies for the decomposition on the substrate. This situation can be improved using organometallic or metal-organic precursors. There are several design strategies exploited to have compounds with high vapor pressure: first of the entire precursor (solid or liquid) should be monomeric.

This is sometimes achieved using bulky functional groups on the ligand, which allows the intermolecular distance to be increased, thus decreasing intermolecular forces. Another strategy often used is the introduction of fluorinated ligands, such as the popular bidentate hexafluoro acetylacetonato. The strong carbon-fluorine bond is much less polar than the carbon-hydrogen bond, giving a lower contribution to the molecular polarizability, which implies reduced intermolecular forces. Of course, the main drawback of this approach is the possibility of having undesired fluorine incorporation in the film. In any case, a detailed understanding of the structure volatility relationship is

still lacking, since many factors are involved Aromatic functional groups on the ligand system should be avoided because of the strong intermolecular stacking interaction that they exert. Ideally, a CVD precursor should not be too air-sensitive, a frequent problem with metal-organic compounds. Air sensitivity is sometimes problematic because it makes the handling and storage of the compounds more difficult. It could also be detrimental during the deposition process (unless we want to deposit metal oxides). A way to decrease air sensitivity is to have a saturated coordination sphere around the metal center, in order to reduce the reactivity towards water or oxygen. The mechanism of decomposition of the precursor on the substrate is a particular characteristic of the molecule being used and is often a difficult matter to predict. Several experimental and theoretical studies have been carried out so far to address this important issue, but we are still far from being able to predict, *a priori*, the decomposition pathway for a given precursor. A liquid precursor is always the best situation since the transport from the evaporator system to the reactor can be easily controlled. In contrast a solid precursor might lead to an irreproducible evaporation rate, due to the variation of the exchange surface between the carrier gas and precursor during the process.

The deposited material synthesized in surface reaction in CVD posses an intrinsic advantage over physical deposition process such as sputtering in its ability to produce thin layer of material with conformal coverage over small diameter, high aspect ratio device features. This capability has become increasingly important as feature size on integrated circuits (ICs) decrease with successive device generations. The demand for CVD route to a variety of materials has in turn, generated interest in the design of precursors.

## CASES STUDIES IN CVD PRECURSORS FOR METAL OXIDES

Bulk single and polycrystalline magnesium aluminum spinel,  $MgAl_2O_4$  is widely recognized for its infrared transmission characteristics, excellent mechanical and thermal shock resistance, and chemical durability. Epitaxial films have been prepared from the vapor phase using the Al-HCl-MgCl<sub>2</sub>-CO<sub>2</sub>-H<sub>2</sub> system for fabrication of silicon-on-insulator (SOI) integrated circuit and as a buffer layer on which to deposit superconductor films. This process requires temperatures between 600 and 800 °C for formation of the volatile metal compounds and growth temperatures around 900 °C. More recently, it was reported<sup>11</sup> that stoichiometric spinel films had been achieved at growth temperatures from 500 to 1000 °C using magnesium dialuminum isopropoxide, a bimetallic precursor with the same 1:2 Mg/Al ratio as the film. This latter process used flash vaporization of a precision metered liquid source composed of 10%  $(Mg[Al(OPr^i)_2])_2$  dissolved in a 9:1 mix of isopropyl alcohol: tetraglyme. A 3:1 oxygen and argon carrier gas was used. The focus of this work was synthesis of an epitaxial buffer layer on which to deposit ferroelectric-based infrared detectors and so focused on the properties at growth temperatures, around 900 °C. Thicker spinel films have also been used as protective layers for zirconia electrolytes in devices such as solid Substrate heater. MOCVD is the process which allows direct vaporization and film growth from a variety of volatile alkoxides, e.g. magnesium dialuminum isopropoxide. Due to the interesting optical and robust mechanical and chemical properties of spinel, it was the matter of interest to explore the possibility of depositing stoichiometric films at reduced temperatures. The deposition and characterization of  $MgAl_2O_4$  films grown at temperatures between

300 and 500 °C using solid  $\{Mg[Al(OPr^i)_2]\}_n$  as the source were studied. Stoichiometric, transparent films were achieved using a pure argon carrier without the introduction of additional oxidant into the system.

The moisture sensitive  $\{Mg[Al(OPr^i)_2]\}_2$  prepared, as described in the literature,<sup>1</sup> by the reaction of Mg with 2 equiv of  $Al(OPr^i)_3$  in isopropyl alcohol. Although pure  $Mg[Al(OR)_4]_2$  is a volatile liquid, experiments show<sup>1</sup> that freshly distilled  $Mg[Al(OPr^i)_3]$  becomes solid over several minutes. The solidification is believed to result from dimerization of the  $Mg[Al(OPr^i)_3]$  to  $\{Mg[Al(OPr^i)]\}_2$ . At room temperature the polymeric form is favored and the material is solid. However, by about 100°C, the equilibrium is shifted toward the liquid monomer which distills at about 105-109 °C at a pressure of 0.1-0.2 Torr. In the MOCVD experiments, samples of solid  $\{Mg[Al(OPr^i)_4]_2\}$ , were weighed in a dry box and transferred to the MOCVD apparatus under high-purity dinitrogen. The sample was loaded into the apparatus under a stream of argon gas. Films were then deposited via the procedures described below. Glassy  $MgAl_2O_4$  films were deposited using a modified bell-jar type evaporation system. The substrates were mounted about 20 cm above the alkoxide source. A radiant heater fabricated from a serpentine strip of NiKovar sandwiched between two sheets of Vycor was used to heat the substrates to as high as 500 °C. The substrate area was typically 25 cm<sup>2</sup> while the total heated area subject to film growth was 80 cm<sup>2</sup>. The metal alkoxide precursor was loaded into a 2.5 cm diameter alumina crucible which was inserted into a resistance ring heater for vaporization. A 0.64 cm diameter stainless steel line with 1.0 mm perforations.

Lanthanum aluminium oxide ( $LaAlO_3$ ) has a range of potential advanced materials applications. In the crystalline form,  $LaAlO_3$  has a layered perovskite-type structure with alternate Al–O<sub>2</sub> and La–O layers comprising the lattice units,<sup>2</sup> and offers the possibility of epitaxial growth on Si,<sup>3</sup>  $SrTiO_3$ ,<sup>4</sup> and other substrates.<sup>5,6</sup> The structural compatibility of  $LaAlO_3$  with other multicomponent oxides makes it a potential substrate, or buffer layer, for a variety of perovskite films such as high temperature superconductors, ferroelectrics, metal-conducting oxides and colossal magnetoresist oxides.<sup>7</sup> Recently,  $LaAlO_3$  has also attracted much attention as an alternative to conventional  $SiO_2$  gate dielectric in sub-0.1 mm complementary metal-oxide-semiconductor (CMOS) devices.<sup>8</sup> The continual miniaturization, or scaling in the dimensions of the field effect transistor (FET) has forced the channel length and gate dielectric thickness to also decrease rapidly, and as the dimensions of the  $SiO_2$  layer approach 2–3 nm, direct electron tunnelling and high leakage currents present serious obstacles to future device reliability. The use of materials with a higher dielectric constant (k) than  $SiO_2$  allows an equivalent capacitance to be achieved in a physically thicker insulating layer, and remarkable device results have been obtained using  $La_2O_3$  gate dielectric layers (k of  $La_2O_3$  5 30 compared with k 5 3.9 for  $SiO_2$ ), and a  $La_2O_3$  layer of 33 Å gave a  $SiO_2$  equivalent thickness as low as 0.48 nm together with very low leakage currents.<sup>9</sup> However, uncapped  $La_2O_3$  in its binary form is chemically unstable and  $La_2(CO_3)_3$  forms readily during growth or upon storage or annealing,<sup>10,11</sup> and  $La_2O_3$  is easily converted to  $La(OH)_3$  on reaction with ambient water.<sup>11,12</sup>  $LaAlO_3$  combines the advantages of the high permittivity of  $La_2O_3$  with the chemical and thermal stability of  $Al_2O_3$ .  $LaAlO_3$  retains a relatively high permittivity of <sup>13,14</sup> and has a large band gap of 6.2 eV,<sup>15</sup> and high band offsets on Si (1.8 eV for electrons and 3.2 eV for holes).<sup>15</sup> In addition,  $LaAlO_3$  generally remains amorphous during annealing

during CMOS processing.<sup>13</sup> This leads to a reduction in leakage currents compared with polycrystalline dielectric films and inhibits the formation of a low permittivity SiO<sub>2</sub> layer at the Si/LaAlO<sub>3</sub> interface. Consequently, equivalent SiO<sub>2</sub> thicknesses as low as 0.9–1.1 nm have been achieved using LaAlO<sub>3</sub>.<sup>16</sup> LaAlO<sub>3</sub> films have been deposited by a variety of techniques including molecular beam epitaxy (MBE),<sup>15</sup> pulsed laser deposition,<sup>16</sup> magnetron sputtering,<sup>17</sup> sol-gel techniques,<sup>18</sup> atomic layer deposition (ALD),<sup>19,20</sup> and metal organic chemical vapour deposition (MOCVD).<sup>21,22</sup> The La and Al precursors used in ALD include La(thd)<sub>3</sub> (thd 5,2,2,6,6-tetramethylheptane-3,5-dionate),<sup>11</sup> La[N(SiMe<sub>3</sub>)<sub>2</sub>]<sub>3</sub>,<sup>20</sup> La(Pr<sup>i</sup>AMD)<sub>3</sub> (Pr<sup>i</sup>AMD 5-N,N9-diisopropylacetamidinate)<sup>19</sup> and AlMe<sub>3</sub>,<sup>19,20</sup> whilst the most commonly used precursors used in MOCVD are the β-diketonates La(thd)<sub>3</sub> and Al(thd)<sub>3</sub>.<sup>21,22</sup> The advantages of using alkoxide precursors rather than β-diketonates include lower deposition temperatures and reduced carbon contamination,<sup>23</sup> whilst the use of a single source precursor containing the metals in the ratio required in a complex solid oxide offers the potential of improved stoichiometry control, especially in the growth of complex oxides by liquid injection MOCVD where the use of a single evaporator generally necessitates careful matching of precursor evaporation and deposition characteristics.<sup>24</sup>

The complex [LaAl(OPr<sup>i</sup>)<sub>6</sub>(Pr<sup>i</sup>OH)]<sub>2</sub> was synthesized from the reaction of 1 mol. equiv. of LaCl<sub>3</sub>·3Pr<sup>i</sup>OH with 1 mol. equiv. of freshly prepared KAl(OPr<sup>i</sup>)<sub>4</sub> in refluxing toluene. To this were added 2 mol. equiv. of freshly prepared KOPr<sup>i</sup> and the reaction completed by refluxing. Separation from precipitated KCl was followed by the removal of volatiles in vacuo and recrystallisation from pentane which yielded colourless crystals of [LaAl(OPr<sup>i</sup>)<sub>6</sub>(Pr<sup>i</sup>OH)]<sub>2</sub>. The complex was characterised by elemental microanalysis, IR spectroscopy, NMR spectroscopy and an X-ray structure determination. Like the related isostructural Er,<sup>25</sup> Nd<sup>26</sup> and Y<sup>27</sup> complexes, [LaAl(OPr<sup>i</sup>)<sub>6</sub>(Pr<sup>i</sup>OH)]<sub>2</sub> is a centrosymmetric dimer with 6-coordinate La and 4-coordinate Al atoms. The two La atoms are linked by two bridging isopropoxide ligands, and each La atom is linked by a further two bridging isopropoxide ligands to an Al atom. The coordination geometry at La is highly distorted octahedral, with cis O–La–O angles ranging from 60.11(17)° to 111.8(2)°. La–O distances range from a maximum of 2.647(5) Å for La(1)–O(3) (the Pr<sup>i</sup>OH ligand) to a minimum of 2.184(6) Å for La(1)–O(2) (the terminal isopropoxide ligand). The La–O–La bridges show slightly shorter La–O distances (2.421(5) Å and 2.424(5) Å) than the La–O–Al bridges (2.530(6) Å and 2.564(5) Å). The 4-coordinate Al atoms show distorted tetrahedral geometry with O–Al–O angles ranging from a minimum of 91.5(3)° to a maximum of 119.4(3)°. As expected the Al–O distances are shorter for terminal isopropoxide ligands (1.708(7) Å and 1.746(6) Å) than for bridging isopropoxides (1.775(6) Å and 1.787(6) Å).

Gallium oxide (Ga<sub>2</sub>O<sub>3</sub>) is an electrical insulator at room temperature and semiconducting above 500 °C.<sup>28</sup> It is thermally stable and adopts a monoclinic (β-Ga<sub>2</sub>O<sub>3</sub>) structure. The formation of Ga<sub>2</sub>O<sub>3</sub> thin films is of interest as it is an ideal material for application as a thin-film gas sensor at high temperatures and in optoelectronic devices.<sup>29,30</sup> It is particularly attractive for use as a gas sensor as the function of the sensor could be switched with temperature. Thus, below 900 °C, gallium oxide thin film operates as a surface-control-type sensor to reducing gases, for example ethanol and CO.<sup>31,32</sup> At temperatures above 900 °C the electric conductivity changes depend on the concentration of oxygen,

therefore oxygen concentration can be monitored. Oxygen gas sensors have practical use in monitoring and controlling oxygen concentrations in waste gases, chemical processes and exhaust gases of automobiles.<sup>32-34</sup> Gallium oxide films also have potential practical uses outside of sensors, such as a new phosphor host material for thin film electroluminescent (TFEL) devices<sup>35-37</sup> and as catalysts because of their high ion-exchange selectivity and capacity.<sup>38-41</sup>

Gallium oxide thin films have been grown by single-source chemical vapour deposition (CVD) using a range of precursors. These include homoleptic gallium tris(alkoxides),<sup>42-43</sup> gallium fluoroalkoxides<sup>44</sup> and gallium tris(hexafluoroacetylacetonate).<sup>44-45</sup> The presence of fluorine in some of the precursors could result in fluorine contamination in the Ga<sub>2</sub>O<sub>3</sub> films, which could cause problems for gas sensor applications, due to baseline resistance and sensor drift. The precursors [ClGa(OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)<sub>2</sub>] and [Me<sub>2</sub>Ga(OC(CF<sub>3</sub>)<sub>2</sub>CH<sub>2</sub>NHtBu)] have also been used to prepare Ga<sub>2</sub>O<sub>3</sub> thin films in the presence of O<sub>2</sub> at 500–600°C *via* MOCVD. However, a multi-step synthetic route was involved to prepare the ligands, which is unsuitable for scale-up operations. The gallium mono(alkoxide) [Et<sub>2</sub>Ga(OCH<sub>2</sub>CH<sub>2</sub>NMe<sub>2</sub>)]<sub>2</sub> resulted in the formation of oxygen deficient gallium oxide films.<sup>46,47</sup>

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