Low-temperature Fabrication of Aluminium Oxide Thin Films

by

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Abstract

Chemical and structural characteristics of aluminium oxide (Al₂O₃) exhibit key properties of the material. Metastable γ, δ and θ-Al₂O₃ are important in catalytic industry, gas-sensing and optical devices. These transitional phases can be converted to the thermally stable α phase, which has a hexagonal close-packing structure and exhibits excellent thermal stability, chemical and wearing resistance, and rigidity.

Processing conditions for crystalline films can vary depending upon the degree of crystallinity required. Typical formation of θ-Al₂O₃ from boehmite (γ-AlOOH) by heating requires a significantly high temperature exceeding 800°C.

This thesis reports the fabrication of Al₂O₃ thin films on Si <1 0 0> wafers at a temperature of 500 °C (amorphous) and 550°C (crystalline). This was achieved through a unique approach utilising a novel single-source chemical vapour deposition (SSCVD) technique. The precursor was designed to have structurally octahedral Al-O cores enshrouded by large carbamate ligands, which increase the molecule’s volatility but are easily removable upon decomposition. It also showed the growth orientation α <1 1 3> formed at 10⁻⁶ Torr was different from δ <4 0 0> formed at 10⁻² Torr, suggesting the thermally stable phase was produced at a lower background pressure.

For comparison, a solvothermal approach using the same precursor in a high pressure autoclave produced Al₂O₃ thin films at temperatures as low as 65°C. The low-temperature decomposition of aluminium diisopropyl-carbamate was elucidated to be via the β-elimination of the carbonate ligand. A range of similar precursors such as aluminium diethylcarbamate,
aluminium dibutylcarbamate, and aluminium di-sec-butylcarbamate were subsequently synthesised using Schlenk chemistry and analysed.

In an inorganic sol-gel approach, Al(NO$_3$)$_3$ was used as an Al$^{3+}$ source in an aqueous (or glycerol) solution. OH$^-$ ions generated by the urea hydrolysis enhanced the production of Al(OH)$_3$, formed an amorphous film on the Si substrate. By combining a high-pressure hydrothermal technique, the hydroxide film was then demonstrated to convert to a polycrystalline Al$_2$O$_3$/AlOOH film at an overall temperature of 200°C. In addition, the hydrothermally treated films appeared as a densely packed and uniform surface, in contrast to crack formations by a conventional annealing treatment.

All deposited films were investigated using a range of laboratory and synchrotron based analytical techniques. These included X-ray photoelectron spectroscopy and diffraction and near edge X-ray absorption fine structure spectroscopy.
Declaration

_This is to certify that_

i. the thesis comprises only my original work towards the PhD except where indicated in the Preface,

ii. due acknowledgement has been made in the text to all other material used,

iii. the thesis is less than 100,000 words in length, exclusive of tables, bibliographies and appendices as approved by the RHD Committee.

Xiaofei Duan
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To Mum, Dad and Juan, with all my love

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Publications


Conferences

1. The 56th American Vacuum Society International Conference, San Jose, USA, 2009
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2. The Asia-Oceania Forum for Synchrotron Radiation Research, Melbourne, Australia, 2008
   Poster presentation on the topic “NEXAFS study of the structural evolution of polycrystalline and amorphous Al₂O₃ thin films”
3. The Australian Research Network for Advanced Materials, Canberra, Australia, 2007
   Oral presentation on topic “Highly oriented aluminium oxide thin film growth via chemical vapour deposition of novel single-source precursors”
Glossary

ADIC   Aluminium(III) diisopropylcarbamate
ADEC   Aluminium(III) diethylcarbamate
ADBC   Aluminium(III) dibutylcarbamate
ADSC   Aluminium(III) di-sec-butylcarbamate
Alisop  Aluminium(III) triisopropoxide
Alacac  Aluminium(III) triacetylacetonate
Alact   Aluminium(III) triacetate

TGA     Thermogravimetric analysis
XPS     X-ray photoelectron spectroscopy
XRD     X-ray diffraction
SEM     Scanning electron microscopy
NEXAFS  Near edge X-ray absorption fine structure spectroscopy
IR      Infra-red spectroscopy
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Chapter 1

Introduction

1.1 Background and Aims

Aluminium oxide (Al\textsubscript{2}O\textsubscript{3}), also known as alumina, is commercially extracted and produced from bauxite, which is an abundant ores, via the Bayer process. Al\textsubscript{2}O\textsubscript{3} resembles white powder (amorphous and polycrystals) or colourless hexagonal single crystals with a melting point of around 2020°C.\textsuperscript{[1]} It is insoluble in water and organic liquids but very slightly soluble in acids and alkalis. Al\textsubscript{2}O\textsubscript{3} is a remarkable material that can exhibit chemical resistance together with good thermal stability. Coating such materials as thin films can transfer these properties to protect other materials.

A number of physical and chemical techniques have been reported \textsuperscript{[2-7]} for the fabrication of Al\textsubscript{2}O\textsubscript{3} thin films. Such fabrication techniques usually require high deposition temperatures, ranging from 800 to 1200 °C depending on the formation of crystalline structures.\textsuperscript{[8]} This limits its application as coatings to substrates that can withstand such high temperature processing conditions.

The aim of this project is to explore methods for making thin film Al\textsubscript{2}O\textsubscript{3} with a degree of crystallinity that will enable key properties of the bulk oxide
material but at lower processing temperatures.

1.2 Crystal structures and transitions

$\alpha$-$\text{Al}_2\text{O}_3$ exists in several crystalline phases. These phases can be divided into two categories, according to their respective stability: thermally stable and metastable.

$\alpha$-$\text{Al}_2\text{O}_3$ is the most thermally stable phase. It has a trigonal Bravais lattice with a space group of R-3c. The oxygen ions form a hexagonal close-packed (hcp) lattice with spacing parameters $a = 4.75$ Å and $c = 12.9$ Å (Inorganic Crystal Structure Database, Reference code 01-071-1128). Each O is bonded to four Al in the form of a distorted tetrahedron and each Al is bonded to six O in the form of a distorted octahedron.[9] This structure can be determined as identical layers stacked in alternating fashion (i.e. ABAB...) (Fig. 1).

![Diagram of hcp and fcc structures](image)

Figure 1. Hexagonal close packing (hcp) and face-centred cubic (fcc) structures.
Other crystals, including γ, δ and θ phases, fall into the metastable category. Ultimately, they can all transform to the most stable α phase at elevated temperatures. These phases contain face-centred cubic (fcc) packing of oxygen anions with aluminium cations distributed over octahedral and tetrahedral sites. The fcc structure can be described as alternating layers ABCABC... (Fig. 1).

γ-Al₂O₃ has been described as a defect cubic spinel structure (AB₂O₄) with vacancies on 24 cation positions. The symmetry of the spinel structure is described by the Fd3m space group. 32 O anions form an fcc lattice with the parameter a = 7.9 Å. 64/3 Al cations are in tetrahedral and octahedral sites to fulfil stoichiometry.

δ-Al₂O₃ has been described as a superlattice of the spinel structure γ-Al₂O₃ with ordered cation vacancies. It has an orthorhombic structure with the lattice parameters a = 7.9 Å, b = 15.8 Å and c = 11.9 Å. A tetragonal structure (a = b = 7.9 Å) is also reported. The δ supercell has a tripled unit cell of the spinel with 96 O anions and 64 Al cations per unit cell.

θ-Al₂O₃ contains monoclinic symmetry (space group C2/m) which is a structural isomorph of β-Ga₂O₃. The unit cell has the lattice parameters a = 11.9 Å, b = 2.8 Å and c = 5.6 Å. The structure is evolved from γ-Al₂O₃ with ordered cations. It contains 20 ions, with eight Al cations occupying four octahedral and four tetrahedral coordination sites.
Transitions

The transformation of crystalline Al₂O₃ based on transformation temperatures is illustrated in figure 2. The dehydroxylation of monoclinic gibbsite (γ-Al(OH)₃) results in orthorhombic boehmite (γ-AlOOH) at 60 – 300 °C.[16] The subsequent transformation route can be described as γ → δ → θ → α phase.[8] Other approaches by heating crystalline aluminium hydroxide, especially diaspore (α-AlOOH) require lower temperature to form α-Al₂O₃.[8]

Figure 2. Sequential phase transformation towards stable α-Al₂O₃ with respect to formation temperatures.[8]

1.2 Al₂O₃ coatings

Amorphous Al₂O₃ coating

Aluminium oxide naturally occurs on the surface of aluminium. Metallic aluminium is very reactive to atmospheric oxygen, whereby a thin passivation layer of oxide forms very readily. The amorphous (long-range structurally disordered) oxide coating is responsible for metallic aluminium's resistance to further weathering. Depending upon the ambient
conditions, an amorphous Al$_2$O$_3$ layer up to 5 nm in thickness can form after exposure.\textsuperscript{[17]} The Pilling-Bedworth ratio for Al$_2$O$_3$/Al is 1.29,\textsuperscript{[18]} indicating a higher volume of the oxide than the volume of the metal. Thus it helps provide the metal surface with a barrier layer that reduces the rate of any further oxidation.

Coatings of Al$_2$O$_3$ are also strongly resistant to corrosion and erosion. Cavitation erosion experiment performed by Pflitsch et al.\textsuperscript{[19]} (according to the ASTM G32-92 standard) showed that the erosion rate of an amorphous alumina film (0.75 μm thick) on a steel surface was three times slower than a clean uncovered steel, due to good adherence and wear resistance of the coating to the metal surface.

**α-Al$_2$O$_3$ coating (stable)**

The natural occurrence of α-Al$_2$O$_3$ is known as corundum which consists of near-pure Al$_2$O$_3$. Corundum is found in the precious gemstones ruby and sapphire. Trace elements Fe$^{3+}$ and Cr$^{3+}$ in ruby induce a red appearance, while all other colorations fall under the designation sapphire. Corundum exhibits remarkably high hardness (9.0 on the Mohs scale) and is the second-hardest crystalline mineral after diamond (a cubic close-packing of carbon).\textsuperscript{[1]}

The hexagonal close-packing of aluminium and oxygen ions within α-Al$_2$O$_3$ leads to its exceptional mechanical properties. Coatings of α-Al$_2$O$_3$ provide excellent wear endurance and rigidity.\textsuperscript{[20,21]} Applications vary from polishing abrasives to protective coatings on cutting tools. The maximum hardness of α-Al$_2$O$_3$ can be as high as 23 GPa.\textsuperscript{[22,23]} Furthermore, α-Al$_2$O$_3$, with its excellent physical properties, is a significant implantation material, for use in such applications as synthetic teeth and hip joints in comparison with
metal materials.\textsuperscript{[24,25]} Coatings of α-Al\textsubscript{2}O\textsubscript{3} have also replaced polyethylene for use in total hip replacements and joints.\textsuperscript{[26,27]}

\textit{Transitional Al\textsubscript{2}O\textsubscript{3} coatings (metastable)}

Structural defects within transitional Al\textsubscript{2}O\textsubscript{3} result in lower rigidity and thermal stability than those of α phase, but these metastable Al\textsubscript{2}O\textsubscript{3} crystals are of importance in catalytic and optical applications.

γ-Al\textsubscript{2}O\textsubscript{3} is mainly applied in catalytic and petrochemical industries, \textsuperscript{[28,29]} as a catalytic supporter, due to its high surface area and acidity. The surface acidity of γ-Al\textsubscript{2}O\textsubscript{3} facilitates the dispersion of basic metal oxides, which interacts with the acidic site of γ-Al\textsubscript{2}O\textsubscript{3}, thus the catalytic activity increases.

Due to the structural similarity to γ-Al\textsubscript{2}O\textsubscript{3}, there are few reports on the application of δ-Al\textsubscript{2}O\textsubscript{3}. More \textit{et al}.\textsuperscript{[30]} reported the use of δ-Al\textsubscript{2}O\textsubscript{3} films with 1 wt.% of Cu\textsubscript{2}O on α-Al\textsubscript{2}O\textsubscript{3} substrates in detecting H\textsubscript{2} gas at ppm levels.

The optical property of θ-Al\textsubscript{2}O\textsubscript{3} (refractive index 1.73) is very close to the α-Al\textsubscript{2}O\textsubscript{3} phase (refractive index 1.76).\textsuperscript{[1]} It allows Al\textsubscript{2}O\textsubscript{3} coating on optical devices to concentrate visible light while maintaining transparency. Indirect band gap of θ-Al\textsubscript{2}O\textsubscript{3} is 1.6 eV smaller than that of α-Al\textsubscript{2}O\textsubscript{3} and the energy loss function of θ-Al\textsubscript{2}O\textsubscript{3} is about 1 eV lower than that in α-Al\textsubscript{2}O\textsubscript{3}.

The application of Al\textsubscript{2}O\textsubscript{3} in electrical devices is due to its high dielectric constant (κ) of 9 and a band gap of 8.8 eV.\textsuperscript{[1]} However, Al\textsubscript{2}O\textsubscript{3} crystalline structure for such uses is not specified. Al\textsubscript{2}O\textsubscript{3} is used to replace the ubiquitous SiO\textsubscript{2} (κ~3.9 and band gap ~9 eV) \textsuperscript{[1]} as a gate oxide for improved current suppression,\textsuperscript{[31-34]} such as CMOS devices, graphene-based transistors \textsuperscript{[35]} and insulation coating on carbon nanotube.\textsuperscript{[36]} Al\textsubscript{2}O\textsubscript{3} is also
used in the construction of radio-frequency transmission lines, where its increased dielectric constant enables the lines to be made into capacitors with reduced physical volumes. Mauro et al.\cite{37} and Yadavalli et al.\cite{38} used Al$_2$O$_3$ as a dielectric material in capacitors and as tunnel dielectrics, leading to the development of transistors in single-electron memory devices, and as a replacement for inter-poly O-N-O dielectric in flash non-volatile memories. Though the structural perfection of crystalline $\alpha$-$\text{Al}_2\text{O}_3$ leads to a minimum dielectric loss, this leads to the best material in radio-frequency and microwave communication.\cite{39}

1.3 Why low-temperature chemical methods?

Applying crystalline aluminium oxide can add additional physical properties to a system. In particular, $\theta$-$\text{Al}_2\text{O}_3$ exhibits good rigidity and low dielectric loss. However, the transformation of $\theta$-$\text{Al}_2\text{O}_3$ from aluminium hydroxide by heating requires high-temperature ($> 800 \, ^\circ\text{C}$) processing.\cite{8}

Annealing is a conventional method by heating both a film and its substrate at elevated temperatures, in order to transform an amorphous structure to a crystalline phase. During heating of amorphous films, crack formation often occurs for cases with differential sintering leading to strain incompatibilities,\cite{40,41} and cracks develop from intrinsic defects.

In methods that deposit films directly onto a heated substrate, crack formation and decohesion can also develop during the cooling phase of heated films and substrates. This is a consequence of differences between the thermal expansion coefficients of the substrates and the coated films.\cite{42} In addition, a high processing temperature can change the properties of many substrates, especially their structural characteristics.
The advent of a low-temperature technique would provide Al₂O₃ coatings to a wide range of substrates with low melting points. The synthesis of crystalline Al₂O₃ thin films is explored in the thesis.

1.4 Approaches to low-temperature fabrication of Al₂O₃ crystalline phase

There have been many reports chemical deposition of Al₂O₃ thin films. Deposition techniques include physical vapour deposition,[43] chemical vapour deposition (CVD),[44] atomic layer deposition,[45] and sol-gel deposition.[46] In addition, post annealing is often employed to form crystalline phases or improve crystallinity. This in itself raises the overall process temperature. The exploration of chemical approaches becomes challenging.

Three chemical deposition methods are the focus of this study of low-temperature deposition of crystalline Al₂O₃ thin films.

1.5 Chemical vapour deposition

Chemical vapour deposition (CVD) is a popular process in the production of Al₂O₃ thin films. The main step is the development of a suitable precursor. Literature indicates that initial research focussed on the production of Al₂O₃ using separated aluminium and oxygen sources. A common inorganic aluminium source is AlCl₃ and oxygen is typically derived from O₂, H₂O or H₂/CO₂.[47] A vaporised mixture of starting materials undergo hydrolysis and dehydroxylation reactions to produce Al₂O₃ (Eq.1).[44]

\[
2\text{AlCl}_3 + 3\text{H}_2\text{O} \rightarrow \text{Al}_2\text{O}_3 + 6\text{HCl} \quad \text{Eq.1}
\]
A significant drawback of this technique is the difficulty of neutralising gaseous byproducts, that is, corrosive HCl and toxic CO. Due to the non-volatile nature of AlCl₃ and its toxic byproducts, a liquid precursor aluminium trimethyl (Al(CH₃)₃) was used to replace AlCl₃ as the Al donor. The high volatility of Al(CH₃)₃ facilitated the formation of vapour at low pressure without heating. The reactivity of Al(CH₃)₃ was more vigorous due to a weaker bond of Al-C than Al-Cl. Oxygen sources were O₂ and NO. Ehle proposed the formation of Al₂O₃ in equation 2:

\[
2\text{Al(CH}_3\text{)}_3 + 12\text{O}_2 \rightarrow \text{Al}_2\text{O}_3 + 6\text{CO}_2 + 9\text{H}_2\text{O} \quad \text{Eq.2}
\]

However, Al(CH₃)₃ is hygroscopic which causes significant difficulties in handling where exposure to air can cause immediate ignition. Hence, specialised equipments and extreme care are required to manage Al(CH₃)₃.

1.5.1 Single-source chemical vapour deposition

Metal organic precursors, on the other hand, offset the disadvantages of using AlCl₃ and Al(CH₃)₃. The CVD reaction can also be achieved through the decomposition of a single-source precursor. Single-source CVD (SSCVD) is a relatively simple approach that avoids using multiple sources by incorporating all necessary constituents within one precursor molecule. Conventional precursors are aluminium alkoxide and aluminium acetylacetonate. Other precursors, such as aluminium tris-dipivaloylmethanate and aluminium 2-ethylhexanoate, are also reported. These chemicals contain both aluminium and oxygen components. The decomposition process releases Al-O fragments that adsorb onto the surface of targeting substrates. Although a relatively low decomposition
temperature could be achieved at 550 °C, poor quality films containing significant carbon contaminations are obtained.

Previous studies demonstrated low-temperature preparation of high quality ZnO \([58-60]\) and MgO \([61,62]\) thin films using designed zinc or magnesium diethylcarbamate as a single-source precursor. In particular, formation of a crystalline MgO film required a lower decomposition temperature than the film made from conventional magnesium tert-butoxide \([63]\) (450°C compared to 800 °C). A suitable class of compound for SS CVD is carbamates, which are known to undergo low-temperature decomposition under reduced pressure, to produce volatile isocyanate and alcohol fragments that are readily removed in a vacuum.\([64]\)

1.6 Solvothermal reaction (< 150 °C)

Solvothermal reaction is a modified technique from hydrothermal reaction. The water in the hydrothermal reaction is replaced by non-aqueous media. Solvothermal reactions are carried out at a temperature higher than the boiling point of a solvent.

Instances of producing inorganic oxides from organic compounds \textit{via} a solvothermal route have attracted much attention.\([65-68]\) Various metastable crystalline Al\(_2\)O\(_3\) powders were formed at lower temperatures (<300 °C) under solvothermal conditions,\([69-72]\) where these crystals are typically obtained at temperatures >800 °C by post annealing,\([8]\) demonstrating the potential for low-temperature deposition.

In a synthesis route, the decomposition point of a precursor in the liquid phase determines the required temperature, which in most cases is higher
than the boiling point of solvents. The selection of the solvent also depends on whether it is part of the reactants. The chemical properties of solvents discussed here involve boiling point and solubility. In particular, the boiling point of a solvent determines the reaction temperature and internal pressure. Control of the temperature domain is the key objective in solvothermal reactions. Supercritical conditions are often selected for the growth of large crystallites and fine particles, with pressure mainly used for governing in situ dissolution–precipitation mechanisms.

The major disadvantage is the separation of the product (in this case Al₂O₃) from the solvent and the various byproducts of the solvothermal process. Further, problems of incorporation and re-adsorption are increased at such elevated pressure, temperature and concentrated environments. As a result, the chemistry of the precursor becomes very important. Conventional Al precursors such as Al isopropoxide and Al acetylacetate are difficult to utilise at lower reaction temperatures due to their high decomposition point, even under solvothermal conditions.

1.7 Combined sol-gel and hydrothermal deposition (≤ 200 °C)

1.7.1 Sol-gel deposition technique

A sol-gel technique is a wet-chemical methodology typically used in the fabrication of metal oxides. The reaction occurs in a chemical solution in which the precursors construct an integrated network (or gel). Precursors include metal alkoxides or metal chlorides, which undergo hydrolysis and polycondensation reactions. The formation of a metal oxide involves connecting the metal centres with an oxygen (M-O-M) or hydroxide (M-OH-M) link, therefore generating M-O-M or M-OH-M polymers of either discrete
particles or continuous polymer networks in the solution. Thus, the sol evolves towards the formation of a gel-like biphasic system containing both a liquid phase and solid phase.

The sol-gel technique was applied to the deposition of SiO\textsubscript{2} fibres and monoliths via a hydrolysis reaction of tetraethyl orthosilicate.\cite{73} The precursor sol can be either deposited on a substrate to produce films by either dip or spin coating. One distinct advantage of using this technique over vapour-phase processing techniques is that densification is achieved at temperatures as low as 100 °C.

Liquid-phase depositions involve the hydrolysis of precursors such as Al alkoxide to produce hydrated Al(OH)\textsubscript{3} films at temperatures below 100 °C.\cite{74,75} Additional dehydroxylation steps were required in order to form Al\textsubscript{2}O\textsubscript{3} films at temperatures up to 350 °C.\cite{76} Although Al hydroxides were formed, the quality of the film was low due to the limited removal of organic byproducts.

Removal of the remaining solvent requires a drying process, which is typically accompanied by a significant amount of shrinkage and densification. The rate at which the solvent can be removed is ultimately determined by the distribution of porosity in the gel. The ultimate microstructure of the final component will be strongly influenced by changes imposed upon the structural template during the drying process. Thermal treatments are required to vary composition and structure.

The sol-gel approach is a cheap and low-temperature technique that allows for the control of the chemical composition of the product. These films are amorphous and subsequent annealing at temperatures > 800 °C was necessary to obtain the θ phase.\cite{74}
1.7.2 Hydrothermal reactions

Hydrothermal reactions are widely used in geo-science for making single crystals. This method is popular in the production of inorganic oxide compounds. In an aqueous medium, the target material is formed through either synthesis or decomposition under high temperatures and elevated pressures. In conventional hydrothermal methods, the required temperatures and pressures are high, because the method results in a decrease in the melting points of materials at extreme pressures.

The advantages of the hydrothermal method over annealing include the formation of crystallites that are relatively unstable at melting point. The success of hydrothermal treatment in thin film deposition was found in the conversion of polycrystalline ZrO₂ films. This method is a viable alternative for Al₂O₃ crystal growth at relatively low temperatures.

The difficulty of using hydrothermal methods is to monitor the reaction and observe the growth of the crystal. Furthermore, should the film be contaminated prior to crystalline transformation, impurities will remain in the film after the hydrothermal reaction.
1.8 Summary

The introduction chapter reviews crystalline structures of metastable γ-, δ- and θ-Al₂O₃ and their transformation towards the stable α phase. They exhibit remarkable features depending on the degree of crystallinity. In particular, θ-Al₂O₃ with good rigidity and low dielectric loss demonstrates a key application in optical devices.

Various fabrication techniques of Al₂O₃ thin films at low temperature are reviewed. By comparing to these techniques, fabrication of crystalline Al₂O₃ thin films at low temperatures would proceed via three methods: gas phase deposition, liquid phase deposition and sol-gel deposition.

The first approach involves a single-step film deposition using a novel single-source precursor. It includes the decomposition of a carbamate precursor in the vapour phase (chapter 3) or in the liquid phase (chapter 4), and the investigation of the precursors’ thermal properties (chapter 5).

The second approach utilises a multi-step synthesis strategy (chapter 6) in which aluminium hydroxide is made via a urea hydrolysis reaction, followed by thermal dehydroxylation to produce oxides. Hydrothermal treatment is used for polycrystalline transformations at a low temperature of 200 °C.
1.9 References


Chapter 2

Instrumental

2.1 Characterisation techniques utilised in the project

In this chapter, the methods used in the syntheses of precursors and the characterisation of thin films are reviewed. The syntheses of various aluminium oxide precursors were achieved via Schlenk chemistry, and subsequent characterisation was via nuclear magnetic resonance (NMR) and infra-red (IR) spectroscopy. The stabilities of the precursors for SSCVD were assessed initially via thermogravimetric analysis (TGA).

The characteristics of deposited films are outlined in figure 1, including X-ray photoelectron spectroscopy (XPS) for the elemental/chemical compositions of deposited materials; scanning electron microscope (SEM) for surface topography and cross-section of thin films; X-ray diffraction (XRD) for long-range structure and ordering; and synchrotron near-edge X-ray absorption fine structure (NEXAFS) spectroscopy for the local co-ordination of aluminium and oxygen.
2.2 SEM

SEM images the surface of a sample by scanning it with a high-energy beam of electrons in an electron scan pattern. It reveals information about the surface morphology of the film samples.

In a UHV system, an intense electron beam (primary electrons) generated from a cathode ray tube is focused by condenser lenses to a small area on the specimen surface of interest. The primary electrons interact with the sample and emit secondary electrons and back-scattered electrons (BSE) as a result of elastic scattering. These electrical signals are detected and captured by a photomultiplier and used to create images of the scanned area. SEM can produce very high-resolution images of a sample surface, revealing details at the nano-scale.
The morphology and micro-structure of the resulting Al₂O₃ thin films were determined using the Hitachi s900 SEM instrument or FEI Quanta SEM. High-resolution SEM images were obtained at an operational voltage of 4 kV. Due to the low conductive nature of Al₂O₃ that causes scanning faults and image artefacts, Al₂O₃ film samples were coated with a thin layer of chromium to enhance electrical conductivity and improve surface imaging.

2.3 X-ray photoelectron spectroscopy

2.3.1 Fundamental

X-ray photoelectron spectroscopy (XPS) is a surface spectroscopic technique based on the photoelectric effect. Incident X-rays photo ionize electrons from the core orbitals of the various elements present within a sample. These photoelectrons are ejected from the sample surface with unique kinetic energies. The binding energy (BE) of a photoelectron is determined by:

\[ BE = hv - KE \]

Where \( hv \) is the photon energy of the X-rays, \( KE \) is the kinetic energy of the emitted photoelectron measured relative to the Fermi level of the spectrometer.

2.3.2 Instrument and measurement

XPS experiments are carried out on a VG ESCALAB 220i-XL spectrometer (Fig. 2) under ultra high vacuum conditions (a background pressure of 1.3x10⁻⁹ Torr). An aluminium X-ray cathode tube generates photon energy of 1486.6 eV. Ejected electrons are passed through the hemispherical
photoelectron energy analyser and selected at a given energy by electrostatic fields prior to arriving at the detector. The electron intensity is measured as a function of electron kinetic energy at a fixed photon energy.

Precursor powders were adhered to the surface of indium and then mounted on a stainless steel holder. A film sample was mounted onto the holder. The sample was immediately transferred to the analysis chamber through a fast-entry-air-lock (pressure $2 \times 10^{-3}$ Torr) and a high-vacuum preparation chamber (pressure $3 \times 10^{-8}$ Torr) (Fig. 2).
2.3.3 Spectrum

A survey scan reveals any elements presented in thin films. Figure 3 is a survey scan XPS spectrum scan for a reference sapphire (α-Al₂O₃) sample. The spectrum reveals photoemission peaks at binding energies of 531.6, 285.0, 232.8, 169.3, 119.6 and 74.9 eV for O 1s, C 1s, S 2s, S 2p, Al 2s, and Al 2p, respectively, indicating the presence of O, C, S and Al on the surface of α-Al₂O₃. The C 1s peak is calibrated to be 285.0 eV \[2\] as a referencing peak.

![XPS spectrum of the untreated surface of α-Al₂O₃.](image)

The low conductivity of Al₂O₃ causes charging of the film's surface. This effect may broaden spectral lines regardless of the precision built into the instrument. To overcome this problem, effective charge neutralisation is an important process. An electron flood gun (low-voltage electron beam) is used to compensate for this charging effect.
Etching

As newly prepared films exposed to the air, they inevitably adsorb contaminants. Etching was performed to remove the contamination layer of these films. The ion gun filament delivered Ar ions to remove approximately 6 nm of the film’s surface at a pressure of 2.66x10^{-7} Torr. In figure 4, the intensity of the C 1s peak is significantly reduced to 2.1 at%, indicating that the major C content exists on the outer surface of α-Al₂O₃.

![Figure 4. XPS spectrum of the surface of α-Al₂O₃ after Ar+ treatment.](image)

High-resolution XPS spectrum

For a particular element of interest, a high-resolution regional scan can be performed. A narrow energy region is selected, typically ± 10 – 15 eV to the binding energy of its absorption peak, as observed from the survey scan. For
example, a regional scan for C $1s$ is done at a range of 275 – 295 eV. A peak fitting is required to analyse components of carbon.

2.4 Grazing angle X-ray diffraction

2.4.1 Fundamental

XRD is a non-destructive analytical characterisation technique which reveals information about the long-range crystallographic structure, chemical composition, and physical properties of thin films.[8] It also reveals crystallite size (grain size) and preferred orientations in polycrystalline structures. In particular, unknown substances can be identified by comparing diffraction patterns data against a universal database (International Centre for Diffraction Data).

The technique is based on observing the diffraction of X-rays as they pass through a crystalline material. At a particular angle $\theta$, constructive interference, that is, crystalline phases, result in intense diffraction of X-ray beams by the sample.

The scattered intensity of an X-ray beam hitting a sample is a function of both the incident and scattered angle $\theta$. The constructive interference caused by diffraction proceeds according to Bragg’s law:

$$\lambda = 2dsin\theta$$

Where $\lambda$ is the wavelength of the incident X-ray, $d$ (d-spacing) is the separating distance of the reflected lattice-planes and $\theta$ is the incidence angle between the X-ray beam and the sample surface.
2.4.2 Instrument and measurement

The X-ray beam passes through the bulk of a thin film deposited on a substrate. A large background signal would result from a crystal substrate such as the silicon used in this work. Grazing angle XRD is used to characterise the crystallographic structure and preferred orientation of thin films.

XRD testing is carried out using a Philips X’pert MRD or Bruker AXS D8. The instrument is operated at 40 kV and 35 mA, and supplied a Kα emission with a wavelength of 1.5406 Å. Films are scanned for 2θ axis only at a step size of 0.02 or 0.1 2θ°/sec in a continuous scan mode.

2.5 Near Edge X-ray Absorption Fine Structure spectroscopy

2.5.1 Fundamental

NEXAFS is an element-specific electron spectroscopy technique. It is widely used to determine the local co-ordination of the element of interest.[4]

When the X-ray beam scans the sample, absorbed photon energies cause the core electrons to be ejected. The resultant vacancies are then filled by the electrons at higher energy level, resulting in the ejection of Auger electrons (Auger decay). Auger electrons scatter secondary electrons that escape from the sample. When the sample is connected to earth, a drain current is created and measured as total electron yield (TEY).
2.5.2 Instrument and measurement

NEXAFS experiments are conducted on the soft X-ray beam-line (photon energy < 2500 eV) of the Australian Synchrotron. An undulator in the storage ring optimises the beam intensity at various photon energies.

The film samples were mounted on a stainless steel sample holder. The holder was put in the load chamber (pressure 6x10^{-3} Torr), then transferred to the analysis chamber through the transferring chamber (pressure 1.2 x 10^{-9} Torr) (Fig. 5). Thin film samples were characterised in the analysis chamber under a background pressure of 2.6x10^{-10} Torr.

Figure 5. Load chamber and analysis chamber in soft X-ray analysis end-station
A maximum of three film samples could be mounted on the same sample holder (Fig. 6). The holder was inserted using a transfer arm and locked in a manipulator which could position one sample of interest for testing at a time.

![Figure 6. A close view of the sampler holder in the analysis chamber](image)

TEY was measured using a picoammeter and incident photon intensity ($I_0$) was monitored using a gold mesh. A NEXAFS spectrum was plotted as a function of $\text{TEY}/I_0$ against photon energies. The experiments scanned two energy regions of 1550–1630 eV and 520–600 eV for Al and O, respectively.

### 2.5.3. Spectrum

Figure 7 represents the NEXAFS spectra of Al$_2$O$_3$ references in a photon energy range of 1550–1630 eV. Figure 7a is the spectrum of the native Al$_2$O$_3$ layer on pure aluminium. A rapid rise at ~1560 eV is due to the emission of K shell electron of metallic aluminium. The Al absorption peaks are calibrated in the NEXAFS spectra by assuming the K-edge of pure Al metal at photon energy of 1560.0 eV.$^{[2,5]}$ Two absorption peaks at 1566.2 eV and 1571.5 eV indicate the tetrahedral (AlO$_4$) and octahedral (AlO$_6$) co-

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- 29 -
ordinations, respectively. In particular, the AlO4 absorption peak is relative intense than the AlO6 peak.

![NEXAFS spectrum](image)

**Figure 7.** NEXAFS spectrum of (a) amorphous Al$_2$O$_3$ on the Al (>99.9%) surface, (b) $\theta$-Al$_2$O$_3$ and (c) single crystal $\alpha$-Al$_2$O$_3$

The spectrum reveals three absorption peaks in crystalline $\theta$-Al$_2$O$_3$ (Fig. 7b). The absorption peak at 1566.4 eV is less intense than peaks at 1568.6 eV and 1571.8 eV, indicating AlO6 co-ordinations are dominant in $\theta$-Al$_2$O$_3$ structure. Absorption peaks at similar photon energies are also found in $\gamma$-
Al\(_2\)O\(_3\).\[6\] Furthermore, the sharp absorption peak at 1567.9 eV is the only peak in single crystal \(\alpha\)-Al\(_2\)O\(_3\) (Fig. 7c). The detection of a single octahedral co-ordination agrees with the literature that only octahedral co-ordination of Al anions present in \(\alpha\)-Al\(_2\)O\(_3\).\[6\] By comparing the spectra of \(\gamma\), \(\theta\) and \(\alpha\)-Al\(_2\)O\(_3\), it indicates an intensity increase in the peak at \(~\)1568 eV relative to peaks at 1566 eV and 1572 eV, suggesting an increase of AlO6 co-ordination as the temperature raises.

2.6 Schlenk chemistry – preparation of chemical precursors

Schlenk chemistry was developed by W. Schlenk in the early 1920s.\[7\] Schlenk technique is a very useful technique for the synthesis of air- and moisture-sensitive chemicals.\[8\] This technique was employed to prepare the various aluminium dialkylcarbamate precursors that were used for making Al\(_2\)O\(_3\) thin films in Chapters 3 and 4.

2.6.1 Technique

Schlenk glass apparatus is a gas-vacuum dual manifold with four ports (Fig. 8). One manifold connects to the inert gas, which is dried through a drierite cylinder. This is outgased through a paraffin oil bubbler to monitor the gas flux rate. The other manifold connects to a vacuum, which is typically powered by a rotary pump (typical pressure of 3x10\(^{-2}\) Torr). Vacuum gas manifolds often have many ports and lines, and with care it is possible for several reactions or operations to be run simultaneously.

A cold trap (Fig.8) immersed in liquid nitrogen is required when removing gaseous byproducts or evaporating solvent. When the gas/vapours, e.g. benzene, pass through the trap, they are solidified at the bottom of the flask.
The collected chemicals are then disposed in appropriate waste containers. This prevents gaseous chemicals from contaminating the pump and the subsequent release of harmful chemicals to air.

Figure 8. A schematic showing a Schlenk line used in the synthesis of aluminium carbamate precursors.

Siphoning is a process that transfers liquid through a canula between two flasks by differential pressure. The technique avoids contact with air, particularly during transfer, drying and storing. The products of carbamate reactions are aluminium carbamates precursors, which are soluble in benzene and carbamate chloride precipitates. The precursors are air/moisture sensitive, thus the separation of supernatant from precipitates must be achieved in the absence of air. In addition, siphoning supernatant containing benzene (solvent) prevents the exposure of the toxic chemical.

2.6.2 Risks

Schlenk technique deals with low pressure vacuum and high pressure gas using the same manifold. Special awareness of using this technique and
glassware is required. The main risks associated with the use of Schlenk lines are implosions or explosions. An implosion can occur due to flaws in the glass apparatus under high vacuum. An explosion can occur due to the common use of liquid nitrogen in the cold trap, which is used to protect the vacuum pump from solvents. If a reasonable amount of air is allowed to enter the Schlenk line, liquid oxygen can condense into the cold trap as a pale blue liquid. An explosion may occur due to the reaction of the liquid oxygen with any organic compounds also in the trap.

2.7 Thermogravimetric analysis – analysing the precursors’ thermal properties

2.7.1 Fundamental

Understanding the thermal properties of prepared aluminium dialkylcarbamate precursors is important to differentiate the vaporisation point from the decomposition point.

Thermogravimetric analysis (TGA) measures the weight loss of a chemical compound as it is heated. A weight loss in relation to temperature curve can be acquired to analyse these chemical changes and transformations. It was possible to comment on the precursor's thermal stability, as well as the relative volatility of organic by-products from the thermal decomposition process, inferred by examining the percentage weight of the residue left after heating. The sample usually undergoes chemical reactions such as dehydration, sublimation and decomposition at increased temperatures.

Changes in the sample, either exothermic or endothermic, can be detected relative to the inert reference. Thus, a differential temperature analysis
(DTA) curve provides data on the transformations that have occurred, such as sublimation and decomposition. The area under a DTA peak is the enthalpic change and is not affected by the heat capacity of the sample. By subtracting the temperature of the sample from that of the reference, a DTA curve is obtained. The DTA curve indicates the reaction at a certain temperature is exothermic (Tc > 0) or endothermic (Tc < 0).

2.7.2 Instrument and measurement

TGA was performed on a Perkin Elmer TGA 7 or Mettler Toledo model instrument (Fig.9). The instrument consists of a highly accurate set of scales within a small furnace, the system being enclosed within an inert nitrogen atmosphere to minimise the interference of oxidative side reactions.

Prior to the analysis, a precursor sample was dried under vacuum and stored under nitrogen. A small amount of the compound (~10 mg) was transferred in a pre-weighed alumina crucible, which was then suspended within the furnace. Typically, a sample was heated from room temperature to 300°C at a rate of 5 °C/min, then to 800 °C at a rate of 10 °C/min under a
nitrogen atmosphere with a sheath flow rate of 20 ml/min. The analysis is carried out by raising the temperature gradually and plotting weight against temperature. The analyser usually consists of a high-precision scale with a pan loaded with the sample. The pan is placed in a small electrically heated tubular furnace with a thermocouple to accurately measure the temperature. The atmosphere is then purged with an inert gas to prevent oxidation and other undesired reactions.

In DTA mode, the material under study and an inert reference are made to undergo identical thermal cycles, while recording any temperature difference between sample and reference. This differential temperature is then plotted against temperature (thermogram).

Figure 10 shows a typical TGA graph of Al acetylacetonate, which includes three plots against the change of temperatures: the mass of a precursor, the loss rate of the mass and DTA. In figure 10a, the $T_{\text{onset}}$ value was measured by intersecting the tangent of the initial temperature with the slope of most rapid temperature decrease. $T_{\text{onset}}$ is the temperature at which a precursor begins to decompose. Here, $T_{\text{onset}}$ for aluminium acetylacetonate (Alacac) is measured to be ~188 °C. In b, $T_0$ is the point that determines the decomposition of Alacac. This is when the loss rate of a chemical's mass reaches maximum. This value is found at a higher temperature than $T_{\text{onset}}$. $T_0$ is dependent on the ramp rate of temperature. The slower the more accurate. In figure 10c, the DTA curve shows the temperature changes in comparison with an alumina crucible as the reference.
Figure 10. A typical TGA curve shows (a) a function of mass of the sample against temperature and (b) the mass loss rate of the sample at corresponding temperatures. (c) DTA result shows that the decomposition of Alacac is an endothermic reaction.

2.8 Summary

In this chapter, film characterisation techniques are described. These techniques are important in revealing the compositional and structural information of the as-produced Al₂O₃ thin films.

High purity sapphire sample (α-Al₂O₃) was used to provide reference XPS data. The XPS spectrum revealed the photoelectron peaks of O 1s and Al 2p are at the binding energies of 531.6 eV and 74.9 eV, respectively.
NEXAFS experiment used the sapphire sample and high purity Al metal as references. The spectrum showed the detection of the Al K-edge at photon energy 1560 eV in the Al sample. It also showed two absorption peaks at photon energies of 1566 eV and 1572 eV, which indicated tetrahedral AlO4 and octahedral AlO6 co-ordination, respectively. Only one absorption peak (AlO4 co-ordination) was observed at photon energy of 1568 eV in the sapphire (α-Al2O3) sample.

The Schlenk technique for the syntheses of aluminium dialkylcarbamate precursors and TGA for accessing the thermal stability of the precursors are also described.

2.9 References

   The Scienta ESCA300 Database; John Wiley & Sons Ltd, 1992.
[9] Brown, M. E., Introduction to Thermal Analysis · techniques and
Chapter 3

Single-source chemical vapour deposition of oriented \( \text{Al}_2\text{O}_3 \) thin films using aluminium(III) diisopropylcarbamate

3.1 Introduction

This chapter describes the use of aluminium(III) diisopropylcarbamate (ADIC) as a novel single-source precursor for the fabrication of crystalline \( \text{Al}_2\text{O}_3 \) thin films via single-source chemical-vapour deposition (SSCVD). The selected precursor was decomposed at 500 °C under high-vacuum conditions. An \( \alpha <1 1 3> \) oriented \( \text{Al}_2\text{O}_3 \) thin film was formed on a Si wafer at a low temperature of 550 °C.

The aim of this chapter is to examine the compositional and structural characteristic of deposited films and understand the mechanism of precursor decomposition.

An important feature of aluminium carbamates precursor is low-temperature decomposition under reduced pressure, leading to the growth of \( \text{Al}_2\text{O}_3 \) thin films,
3.2 Experimental details

CVD instrumentation

Figure 1 shows the CVD system that was purposely constructed for the growth of Al$_2$O$_3$ thin films by the author. The stainless steel vacuum system includes two units. The vacuum unit consists of an oil pump, a PFEIFFER TPH240 turbo pump, an ion gauge for the measurement of background pressure, a TCP121 turbo controller and a cooling fan. The heating unit consists of a copper stage heated by power supply 1 and a Knudsen cell heated by power supply 2 that is used to vaporise precursors. A thermocouple is employed to measure both the substrate temperature and the sublimation temperature. A Knudsen cell is a hollow copper tube in which one side is screw-capped and 15 mm in diameter, while the other end has a permanent hole of 5mm diameter. The Knudsen cell loaded with precursor powders is mounted in the chamber. The side with a small hole faces the substrate.

A Si <1 0 0> substrate was initially ultrasonicated sequentially in diluted HCl acid, demineralised water then acetone for 10 minutes. The wafer was dried in an oven at 100°C and cooled to room temperature. The wafer was then screwed on a copper stub which was electrically heated. A thermocouple was wired in a copper filament at the bottom of the stage.
Figure 1. The SSCVD chamber used for the fabrication of Al$_2$O$_3$ thin films

Figure 2 is a schematic diagram of the deposition chamber. During deposition, both oil and turbo pump were turned on to reach a required background pressure, which was indicated by an ion gauge. The substrate was heated to reach the required temperature. The Knudsen cell was then heated slowly to approximately 150 °C in order to vaporise the precursor gradually, whilst the temperature of the Si wafer was maintained at a target temperature. The film growth was carried out at substrate
temperatures 450, 500 and 550 °C, while the background pressure remained at ~10^{-6} Torr. The prepared films were labelled as F450-6, F500-6 and F550-6, respectively. The experiments were repeated at the same temperatures, but the background pressure was changed to ~10^{-2} Torr. These films were labelled as F450-2, F500-2 and F550-2, respectively.

Figure 2. A schematic diagram of SSCVD deposition system

3.3 Results and discussion

3.3.1 Film compositions

The resulting films were successfully obtained using aluminium diisopropylcarbamate (ADIC) as a single-source precursor, except at the substrate temperature of 450°C. The obtained film samples were examined using XPS.
Figure 3 shows the XPS survey spectra of precursor ADIC and the untreated surface of film F550-6 made at 550 °C. In the precursor spectrum (Fig. 3a), the peaks of O 1s, N 1s, C 1s, Al 2s and Al 2p photoelectrons are recorded at binding energies of 531.5, 399.4, 285.0, 118.6 and 73.7 eV, respectively, indicating the necessary elements are present in the precursor ADIC. The spectrum of the as-deposited film F550-6 (Fig. 3b) shows peaks of O 1s, C 1s, Al 2s and Al 2p at binding energies of 531.8, 285.0, 119.0 and 75.0 eV, respectively. By comparison, the N 1s peak (BE 399.4 eV) is not detected in the spectrum of film F550-6, indicating the absence of nitrogen component in the film. It suggests the decomposition of the nitrogen-containing carbamate ligand, and byproducts that contain nitrogen are not adsorbed onto the film. The intensity of the C 1s peak in the film also reduced significantly, relative to that of the precursor. In both spectra, the Al 2p and O 1s peaks appear at binding energies of 74-75 and 531-532 eV, respectively. The energy separation between the peaks is 456.8 eV and the O/Al ratio is calculated to be 1.37, in agreement with a previous analysis of Al₂O₃ films.[1].

Figure 3c is the XPS spectrum of the etched surface of film F550-6. The spectrum shows the peaks of O 1s and Al 2p positioned at binding energies of 531.3 and 75.0 eV, indicating the presence of oxygen and aluminium, respectively. The C 1s peak observed in the spectrum of the as-deposited film (Fig. 3b) is absent after Ar⁺ sputtering treatment, confirming the adventitious carbon impurity is primarily on the outer surface of the film. Argon absorption peaks, Ar 2s and Ar 2p, are detected due to the residual Ar⁺ during the etching process.
Figure 3. Survey scan XPS spectra of (a) precursor aluminium diisopropylcarbamate; (b) film F550-6 and (c) the etched film F550-6
3.3.2 Surface contamination

The C 1s peak observed on the untreated surface of film F550-6 (Fig. 3b) was investigated. High-resolution XPS resolved the peak and shows a doublet (Fig. 4a). Three component peaks are fitted at binding energies of 289.1, 286.2 and 285.0 eV, attributing to O-C=O, C-O and C-H bonds, respectively. These surface carbons are common contaminations from hydrocarbons and carboxylic acid when CO₂ reacts with air and moisture.[2,3] The spectrum of carbon is very different from that observed in the precursor. The C 1s in the precursor shows three component peaks at binding energies of 289.2, 286.1 and 284.9 eV, due to carboxyl carbon (O₂C≡N), α-carbon (NCH(CH₃)₂) and β-carbon (NCH(C₆H₅)₂) of the carbamate ligand (Fig. 4b), respectively.

![Graph showing C 1s spectrum of carbon impurities on the surface of film F550-6.](image)

Figure 4a. A high-resolution C 1s spectrum of the carbon impurities on the surface of film F550-6
3.3.3 Depth profiling

A depth-profile XPS spectrum of film F550-6 is shown in figure 5. It has three phases. The first phase is the outer surface of the film and ~6 nm thick. This top layer contains a small amount of carbonaceous contaminations that have been described in the previous section. The second phase is the Al₂O₃ bulk film that is approximately 250 – 260 nm thick. The silicon photoelectron peaks are not detected, indicating a complete coverage of Al₂O₃ thin film on the substrate. The atomic concentrations of oxygen and aluminium remain constant at approximately 58 at% and 42 at% throughout the bulk of the film. Nitrogen content is absent and the concentration of carbon remains below 2 at%.
3.3.4 Proposed deposition mechanism

In CVD, the thermal energy (temperature) needs to be sufficient to break molecular bonds to result in necessary fragments that then adsorb on the surface of the substrate. During deposition, by-product fragments may also adsorb on the surface of the substrate and/or growing films. A higher substrate temperature is required to decompose precursors and remove contaminant to produce high-quality, homogenous films.

XPS results show the absence of the organic fragments of precursor ADIC, that is, containing nitrogen and carbon, throughout the bulk of the film, suggesting a clean decomposition pathway. This pathway suggests that the decomposition of the precursor is complete and separates the Al-O core from
its surrounding ligands. The heated substrate creates a hot boundary above the surface of the substrate and as the precursor decomposes in the hot region, there is no chemical reaction between compound and substrate. The separated, non-volatile Al-O fragments adsorb onto the surface of the substrate and the by-products are removed by vacuum (Fig. 6).

![Figure 6. A proposed SSCVD diagram showing the deposition of Al-O fragments on the surface of a heated substrate](image)

### 3.3.5 Decomposition pathway to pure Al₂O₃

The molecular structure of ADIC \[^{[4]}\] is illustrated in figure 7. Each aluminium atom is octahedrally coordinated by six oxygen atoms (Fig. 7a).
As can be seen from the space-filling model (Fig. 7b), the isopropyl groups enshroud the core of the complex, so inter-cluster polar bonding is not possible. This structural feature, together with the compact globular form of the cluster, should lower intermolecular forces, thus accounting for the significant volatility of ADIC under high vacuum.

![Figure 7. Schematic showing the 3D molecular structure (a) ball and frame (blue – Al; red – O); (b) space-filling (green – Al; red – O; blue - N) of aluminium diisopropylcarbamate](image)

The thermal reaction is dependent on the precursor’s molecular structure and its decomposition temperature. From previous studies on the pyrolysis of carbamates and their derivatives,[5,6] Dyer et al. found that the thermal decomposition of some carbamate compounds occurred at 200 °C under reduced pressure, resulting in the formation of isolated isocyanate and alcohol fragments.[6] These studies enable improved understanding of the thermal decomposition pathway of precursor ADIC.

A proposed decomposition mechanism is illustrated in figure 8. The presence of small, highly charged Al$^{3+}$ species should polarise the attached carbamate ligand, thereby promoting its fragmentation by the loss of oxide ion. The N lone pair and the β hydrogen atom may participate in a β–
elimination reaction. This route would then produce an alkyl isocyanate and propene as fragments.

Figure 8. A proposed β-elimination mechanism for the decomposition of precursor aluminium diisopropylcarbamate
3.3.6 Dependency of film compositions on deposition temperatures

Figure 9 shows the survey XPS spectra of films deposited at various temperatures and pressures. The positions of O 1s and Al 2p photoelectron peaks in the as-deposited films are slightly different from each other. Surface carbonaceous impurities were detected on the outer surface of the films, but not contributing to the composition of the films as they were removed by Ar+ etching. Although Cu was detected in film 500-6, it was also removed by the etching process. In addition, no significant differences were observed between untreated surfaces and etched surfaces. For example, as listed in table 1, the peaks of O 1s and Al 2p on the untreated surface position at binding energies of 531.9 ± 0.1 eV and 74.7 ± 0.2 eV, respectively. The peak position of O 1s on the etched surface is recorded at 531.5 ± 0.2 eV, by assuming Al 2p peaks are unchanged.

Table 1. The binding energies of O 1s and Al 2p of surface composition in films prepared at designed experimental conditions. FWHM of energy absorption peak is in brackets.

<table>
<thead>
<tr>
<th>Films</th>
<th>Reaction conditions</th>
<th>Untreated surface</th>
<th>Etched surface</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>O 1s [eV]</td>
<td>Al 2p [eV]</td>
</tr>
<tr>
<td>550-6</td>
<td>550 °C, 10^{-6} Torr</td>
<td>531.8 (3.16)</td>
<td>75.0 (2.88)</td>
</tr>
<tr>
<td>500-6</td>
<td>500 °C, 10^{-6} Torr</td>
<td>531.9 (3.34)</td>
<td>74.9 (2.94)</td>
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<tr>
<td>550-2</td>
<td>550 °C, 10^{-2} Torr</td>
<td>531.9 (3.34)</td>
<td>74.8 (2.96)</td>
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<tr>
<td>500-2</td>
<td>500 °C, 10^{-2} Torr</td>
<td>532.0 (3.42)</td>
<td>74.6 (2.96)</td>
</tr>
</tbody>
</table>
Figure 9. Survey XPS scans of films deposited at various temperatures and background pressures: (a) 550 °C, 10^{-6} Torr; (b) 500 °C, 10^{-6} Torr; (c) 550 °C, 10^{-2} Torr and (d) 500 °C, 10^{-2} Torr.
Figure 10 shows the binding energy separation between O 1s and Al 2p in the films obtained. A common observation is that the absorption position of O 1s is closer to Al 2p on the etched surface than that on the untreated surface, suggesting that hydroxylated or mixed oxide on the outer surface change to pure oxide in the bulk film. At a hotter substrate surface while maintaining the same background pressure, the energy separation is smaller. At higher background pressure while maintaining the same substrate temperature, the energy separation is bigger.

![Energy separation between O-Al](image)

Figure 10. O-Al separation between binding energies of O 1s and Al 2p.

The O/Al ratios of as-deposited films are also plotted (Fig. 11). The graph shows that the O/Al ratios of the etched surface are greater than those of the untreated surface, suggesting that hydroxylated or mixed oxide on the outer surface changed to pure oxide in the bulk film. At a hotter substrate surface while maintaining the same background pressure, the O/Al ratio is smaller. At higher background pressure while maintaining the same substrate temperature, the O/Al value is bigger.
3.3.7 Film morphology

SEM imaging reveals the surface morphologies of films grown at 500 and 550 °C (Fig. 12). Figures 12a and 12d show the non-cracking morphology of film surface in micro-scale. In addition, a high-resolution SEM image reveals particles with various sizes randomly distribute on the surface of the film deposited at 500 °C (Fig. 12c), whereas smaller particles are more uniform on the surface of the film deposited at 550 °C (Fig. 12e). This indicates an improvement on the surface morphology as the substrate temperature increases. Improvements are also observed in both films’ surface morphologies, comparing to films prepared from aluminium isopropoxide \(^7\) and aluminium acetylacetonate \(^8,9\) in which large particle aggregates were observed. The average thickness of the crystalline Al\(_2\)O\(_3\) film grown using ADIC at 550 °C is 250 nm, obtained after deposition for approximately 2 hours (Fig. 12f). The relatively low growth rate is believed to relate to the low thermal conductivity of Al\(_2\)O\(_3\), which has attenuated heat transfer from the Si substrate to the surface of the growing film.
Figure 12. SEM images show the surface morphology and cross-sectional view of film F500-6 (a) – (c) and film F550-6 (d) – (f).
3.3.8 Long-range crystalline structure

XRD was used to obtain the structural information of crystallites in the as-deposited films. In films F500-6 and F500-2, no diffraction peaks are observed in either experiment (Fig. 13a), suggesting amorphous structures in the bulk of the films. Therefore, the films deposited at 500 °C are amorphous.

Figure 13. XRD diffraction patterns of (a) F500 amorphous films, the as-deposited films (b) F550-6 and (c) F550-2.

In contrast, the films deposited at 550 °C, that is, F550-6 and F550-2, show discernible diffraction patterns as shown in figure 13b and 13c, respectively. A strong peak appears at 43.6 ° (Fig. 13b). This prominent peak is due to
the formation of an oriented Al$_2$O$_3$ <1 1 3> phase. This crystallite orientation is found in α-Al$_2$O$_3$ \cite{10} formed by conventional CVD at a substrate temperature higher than 1000 °C \cite{9,11}. The film F550-2 shows a strong diffraction pattern at 45.5 2θ° (Fig. 13c), which is assigned to orientation Al$_2$O$_3$ <4 0 0>. This crystalline phase is also observed in metastable δ-Al$_2$O$_3$, which is typically obtained from annealing boehmite (γ-AlOOH) at temperatures above 700 °C and is a transitional phase prior to the formation of thermally stable α-Al$_2$O$_3$.\cite{12,13}

By comparison, a single-oriented film is obtained at approximately 850 °C by annealing an amorphous Al$_2$O$_3$ film obtained at 500 °C via SSCVD. Its diffraction pattern shows the formation of a crystalline phase along the <4 0 0> direction (45.9 2θ°), as shown in figure 14. The same diffraction pattern is also observed in the film F550-2, in which the deposition temperature is 300 °C lower.

Figure 14. Diffraction patterns of the film obtained by annealing an amorphous Al$_2$O$_3$ thin film at 850 °C for 2 hours.
Since the [0 0 1] phases have the lowest surface free energy, the planes along the c-axis are formed prior to other orientations. Thus, under thermally activated conditions, that is, annealing, the <4 0 0> plane was grown first. During annealing treatment, diffusion of atoms, the removal of crystal defects and recrystallisation contribute to polycrystalline film formation at excessively high temperatures. The dehydroxylation of hydroxyl on the film’s surface as well as oxidation of impurities may also raise annealing temperature. In contrast, the growth of the <1 1 3> plane suggests a different growth mechanism on the surface of Si substrate. With a pre-organised octahedral Al-O core, this plane has been made at a temperature of 550 °C. Further studies using Synchrotron X-ray absorption techniques will assist the understanding of atomic co-ordination and oxidation states, and therefore enable us to explore the structural evolution of crystal growth in amorphous/crystalline films associated with the precursor’s structure.

3.3.9 Local co-ordination of Al and O ions

NEXAFS studies the local atomic co-ordination of Al₂O₃ in films. Figure 15a is the spectrum of a native Al₂O₃ thin film on a pure aluminium metal as a reference. It reveals the Al K-edge at photon energy of 1560 eV and two absorption peaks at 1566.2 eV and 1571.5 eV, which indicate the tetrahedral (AlO₄) and octahedral (AlO₆) co-ordinations, respectively.[14] In the NEXAFS spectrum of crystalline θ-Al₂O₃ reference (Fig. 15d), two strong Al absorption peaks appear at 1568.6 eV and 1571.8 eV, respectively. It indicates both octahedral co-ordinations are dominant in θ-Al₂O₃ structure. In particular, the peak at 1568.6 eV can only be observed, and differentiated from the peak at 1572 eV, in crystalline Al₂O₃.[14,15]
Figures 15b and 15c are the NEXAFS spectra of films F500-6 and F550-6. Two absorption peaks are observable at 1567.2 eV and 1571.5 eV in either film, indicating both AlO4 and AlO6 co-ordinations present in films prepared via SSCVD. Furthermore, the relative intensity of $I_{\text{AlO6}}/I_{\text{AlO4}}$ in film F550-6 is higher than that in film F500-6, indicating $I_{\text{AlO6}}/I_{\text{AlO4}}$ increases as the temperature increases. It suggests either an increase in AlO6 co-ordination, or a decrease in AlO4 co-ordination, or both. In addition to the XRD results, that film F500-6 is amorphous and film 550-6 is singly orientated, it indicates the long-range ordered structure has a higher ratio of $I_{\text{AlO6}}/I_{\text{AlO4}}$.

Figure 15. NEXAFS spectra showing Al absorption peaks of (a) amorphous Al₂O₃ on the Al surface, (b) film F500-6, (c) film F550-6 and (d) θ-Al₂O₃ film
Figure 16 is the NEXAFS spectra of O absorptions for selected samples. A broadly unresolved absorption peak at 538 – 542 eV is observed in amorphous alumina, showing the native oxide layer on the surface of Al metal which is also reported previously,[14]. In addition, the absorption peak at 541.6 eV appears to be of higher intensity than the shoulder peak at 538.2 eV. This intensity difference is small in the spectrum of $\theta$-Al$_2$O$_3$ (Fig. 16d). In comparison, the O absorption shape in the spectrum of film F500-6 (Fig. 16b) is similar to that of $\theta$-Al$_2$O$_3$, whereas the O absorption shape in the spectrum of film F550-6 (Fig. 16c) is similar to amorphous alumina. The O pre-edges are observed at the same photon energy of 532.2 eV for amorphous Al$_2$O$_3$ (Fig. 16a), film F500-6 (Fig. 16b) and film F550-6 (Fig. 16c). This position is 1.6 eV less than that observed in $\theta$-Al$_2$O$_3$ (Fig. 16d).
Figure 16. NEXAFS spectra showing O absorption peaks of (a) amorphous Al₂O₃ on the Al surface, (b) film F500-6, (c) film F550-6 and (d) θ-Al₂O₃ film

3.4 Summary and conclusion

SSCVD produced single oriented Al₂O₃ thin films at a remarkably low temperature of 550 °C using ADIC as a novel single-source precursor. α <1 1 3> and δ <4 0 0> orientations were obtained at different background pressures. Although the decomposition of ADIC could occur at 500 °C, only
amorphous $\text{Al}_2\text{O}_3$ thin films were formed. The compositional quality and surface morphology of films were substantially improved in comparison with those obtained from conventional aluminium alkoxide and aluminium acetylacetonate precursors.

A decomposition route was proposed for the low-temperature decomposition of ADIC under reduced pressures. The $\beta$-elimination mechanism was the key to the successful SSCVD approach. The decomposition mechanism showed an efficient pathway to remove byproducts, and thus the carbonaceous impurities were minimized.

Future works include focusing on the short-range order characterisation of the films, in order to improve understanding of structural evolution in amorphous/crystalline films.

### 3.5 References

Chapter 4

Solvothermal approach for
low-temperature fabrication of
aluminium oxide thin films

4.1 Introduction

Previously (chapter 3) we saw that the lower temperature limit for SSCVD deposition of crystalline Al$_2$O$_3$ was 550 °C using aluminium(III) diisopropylcarbamate (ADIC) as a single-source precursor.

This chapter utilises the same ADIC precursor, but this time in the high-pressure liquid phase. The decomposition route of ADIC in the liquid phase is studied under solvothermal conditions in order to study the impact of temperature and pressure on the facilitation of the precursor’s decomposition. The growth of stoichiometric Al$_2$O$_3$ thin films is described through a simple solvothermal reaction in which the decomposition of precursor ADIC occurs at a temperature as low as 65 °C.
4.2 Experimental details

An acid digestion bomb (#4745, Parr Instrument Company) was used for solvothermal reactions. This consists of a stainless steel shell and a 23 ml Teflon® cell (Fig. 1)

Figure 1. An autoclave set consists of a stainless steel shell (left) and a removable Teflon® cell (right)

A saturated solution of precursor prepared by dissolving ADIC (60 mg, 6.53 x 10⁻⁵ mol) in dry benzene (1 ml) and was transferred into the Teflon® cell. A clean Si <1 0 0> wafer (10mm x 10mm and 0.25mm thick) was immersed in the solution. The Teflon® cell was then capped and placed in the autoclave. The reaction autoclave was screwed hand-tight and then heated in an oven to the selected temperature for a particular experimental run. The autoclave was allowed to cool after a solvothermal reaction. The Si wafer was removed from the solution and dried at 85 °C to remove benzene. Samples prepared at autoclave temperatures of 65, 85, 105, 125 and 150 °C were labelled as F65, F85, F105, F125 and F150, respectively. The internal pressures created
were calculated by combining the vapour pressures of benzene and air pressures at selected temperatures (Fig. 2). They were calculated to be 1.75 atm at 65 °C, 2.36 atm at 85 °C, 3.32 atm at 105 °C, 4.75 atm at 125 °C and 7.47 atm at 150 °C. Processing times lasted 1, 3 or 6 hours.

Figure 2. Vapour pressures of benzene vs. temperatures chart.[2]

4.3 Thin films prepared at various temperatures

4.3.1 Thin films prepared at temperature > 105 °C

At cell temperatures of 125 °C and 150 °C, a precipitation of dark brown gel in the reaction vessel was observed. The substrate was removed and dried at 85 °C for 1 hour. A brown coating was formed (Fig. 3 inset). This coating was very fragile and could be removed by gently tapping the other side of the substrate.
The surface composition of the gel film was examined using XPS. The spectrum reveals photoemission peaks at binding energies of 532.5, 401.6, 285.0, 269.0, 198.6, 119.4, 99.5 and 74.9 eV for O 1s, N 1s, C 1s, Cl 2s, Cl 2p, Al 2s, Si 2p and Al 2p, respectively (Fig. 3a). This indicates the presence of O, N, C, Cl, Si and Al. The presence of Cl is due to the diisopropylamine chloride produced in the synthesis of precursor ADIC.

Figure 3. Survey scan XPS spectra of the gel film (a) outer surface, (b) after Ar$^+$ etching treatment and (inset) photo image
The nitrogen content, either in the outer surface (Fig. 3a) or in the film (Fig. 3b), is less than 1.5 at%, suggesting the decomposition of precursor ADIC and the removal of N-containing by-products. A high concentration of carbon (56.2 at%) is measured in the outer surface (Fig. 3a) and falls to 9.5 at% after Ar$^+$ etching (Fig. 3b). A Si content of 35.5 at% is detected after Ar$^+$ treatment, suggesting a very thin coating on the Si substrate. In addition, this thin layer has low O and Al concentrations of 23.8 at% and 23.2 at%, respectively.

The solution residue was dried by evaporating off the solvent and was then examined by IR. Figures 4b and 4c show the IR spectra of residues from solvothermal reactions at 65 °C and 125 °C, respectively. Comparing this with the spectrum of precursor ADIC (Fig. 4a) shows the decomposition of the precursor as the absence of C-H stretching at 2800 – 3100 cm$^{-1}$ and organic components at fingerprint region of 400 – 1250 cm$^{-1}$. A broad absorption peak observed at 400 – 1200 cm$^{-1}$ is the Al-O and Al=O stretching,$^{[3-5]}$ indicating the formation of aluminium oxide.
4.3.2 Thin films prepared at temperature ≤ 105 °C

Films are deposited in the liquid phase at temperatures 65, 85 and 105 °C using ADIC as a single source. The film appeared as a blue coating (Fig. 5 inset). The surface compositions of the prepared films were investigated using XPS. Figure 5 is a typical survey scan for film F105. It reveals photoemission peaks at binding energies of 532.5 eV, 285.0 eV, 118.8 eV and 74.9 eV for O 1s, C 1s, Al 2s and Al 2p, respectively, indicating the presence of oxygen, carbon and aluminium.
Nitrogen, which was originally present in the precursor, is absent from the film, suggesting a complete decomposition of the precursor ADIC. The concentration of carbon on the untreated surface is found to be 13.1 at%. The bulk composition of the film is revealed by etching off the outer surface using Ar⁺ (Fig. 5b). The carbon at% is significantly reduced to 1.8 at%, indicating the carbon presented in the untreated surface is not contributing to the composition of the film’s bulk. The oxygen and aluminium contents in the film are 58.5 at% and 39.8 at%, respectively, giving an O/Al ratio of 1.47, in agreement with stoichiometric Al₂O₃.

Figure 5. Survey scan XPS spectra of a) film F105 and b) after Ar⁺ treatment. Inset is a photo image of film F105
4.3.3 Proposed $\beta$-elimination

The solvothermal decomposition pathway in the liquid phase is difficult to elucidate. Dyer et al. have found that the typical decomposition products of carbamate ligands were isocyanate and alkene. A heterogeneous $\beta$-elimination breakdown pathway for ADIC is proposed (Fig. 6). The elimination of $\beta$-hydrogen leads to the removal of isopropene. A pair of electrons, by breaking the C($\alpha$)-N bond, are localised to form a C=N bond that leads to the cleavage of a C-O bond. The electronegative O$^{2-}$ is associated with the eliminated H$^+$ to produce an Al-OH fragment. Sequential dehydroxylation at elevated pressure produces stoichiometric Al$_2$O$_3$. Decomposition of diisocyanate would result in the volatile by-products CO$_2$ and amine.

Figure 6. A proposed $\beta$-elimination of heterogeneous decomposition pathway
4.3.4 Proposed deposition scheme

XPS analysis of the film F105 indicates the absence of nitrogen and carbon, which are originally present in the precursor ADIC. This suggests a complete decomposition pathway that allows the separation of Al-O core from carbamate ligands. The compositions of the films that do not incorporate nitrogen and carbon also suggest that the separated carbamate ligands did not precipitate on the surface of the substrate or the film.

During deposition, the reaction vessel was heated and the solvent started to vaporise (Fig. 7a). This resulted in an increase in the concentration of the precursor (Fig. 7b). The precursor was decomposed via a β-elimnation reaction under solvothermal conditions. Necessary Al-O fragments precipitated and adsorbed on the surface of the substrate (Fig. 7c). The separated by-products were either volatile or soluble in the solvent and were not attributed to the composition of the films.
4.3.5 Solvothermal reaction using aluminium isopropoxide

A β-elimination pathway has also been proposed during the decomposition of metal alkoxides that share similar structural characteristics.[7,8] Hence, a comparative test was carried out using aluminium isopropoxide as a single-source precursor under the same solvothermal conditions. The precursor remained in white suspension and resulted in a white powdery coating on the substrate after drying. The surface compositions of the white coating were investigated using XPS. The spectrum shows the presence of O 1s, C 1s, Si 2s, Si 2p, Al 2s and Al 2p at binding energies of 531.8 eV, 285.0 eV, 154.5 eV, 102.2 eV, 118.6 eV and 74.7 eV (Fig. 8a), respectively, indicating compositions of O, C, Si and Al. After the Ar+ treatment, the C 1s signal has
disappeared (Fig. 8b). This indicates a carbonaceous outer surface, suggesting that C content does not attribute to the bulk of the coating and thus a complete decomposition of the precursor. The SEM image reveals a discontinuous surface morphology that is consistent with the detection of strong Si signals due to a porous surface structure on the Si substrate.

Figure 8. Survey scan XPS spectrum of the produced coating (a) using aluminium isopropoxide and (b) after Ar\(^+\) treatment. Inset shows the surface morphology of the coating.

The surface morphology of a coated substrate (Fig. 8 inset) shows islands of deposited particles. The observation of large surface defects in the SEM
image elucidates the detection of strong Si signals. This experiment shows that films cannot be formed on the Si surface using aluminium isopropoxide.

### 4.4 Effect of changing reaction temperatures

#### 4.4.1 Effects on the film composition

Chemical compositions of films deposited at temperatures of 65, 85 and 105 °C are investigated and compared. When the temperature is maintained at 105 °C, or even lower at 65 °C, Al₂O₃ thin films are formed using ADIC. The O at% is quantified to be 56.3 at%, 57.3 at% and 58.5 at% in films F65, F85 and F105, respectively, showing a linear increase of approx. 1.1 at% per 20 °C. The Al at% also increases slightly, from 39.0 at% in F65, to 39.5 at% in F85 and 39.8 at% in F105. Thus, the O/Al ratios in films F65, F85 and F105 are calculated to be 1.44, 1.45 and 1.47, respectively, as temperatures increase (Fig. 9a). The carbon at% in film F105 is 1.8 at% compared to 3.3 at% in film F85 and 4.4 at% in film F65 (Fig. 9b), indicating less carbonaceous contaminations in films deposited at higher temperatures. The quality of films has been improved at higher deposition temperatures (or pressures).
4.4.2 Effects on the film morphology

Figure 10 shows the surface morphology and cross-sectional SEM images of prepared films at various temperatures. The morphology of film F65 appears as densely packed grains (Fig. 10a). The size of particles ranges from 20 – 25 nm. A film layer is clearly observable on the surface of the Si substrate. This grainy layer has an average thickness of 218 nm. The cross-section of film F65 also shows no preferred growth direction of deposited particles.
Figure 10. Surface morphologies and cross-sections of Al$_2$O$_3$ films prepared at temperatures 65 °C (a-b), 85 °C (c-d) and 105 °C (e-f) for 6-hour reactions.
By comparison with morphologies of films deposited at 85 and 105 °C (Fig. 10c and 10e), the particle size reveals only small differences. Although film thickness varies from 210 nm in film F85 (Fig. 10d) to 346 nm in film F105 (Fig. 10f), the thickness is not dependent on the reaction temperatures.

4. 5 Effect of reaction times

4.5.1 Effects on the film composition

Reactions are run for 1, 3 and 6 hours under solvothermal conditions. The effects of deposition time on the compositions of prepared films are examined. The O at% is quantified to be 57.0 at%, 56.9 at% and 58.5 at% for 1-hour, 3-hour and 6-hour reactions at 105 °C, respectively. The corresponding Al at% increases slightly, from 38.9 at% for a 1-hour reaction, 39.4 at% for a 3-hour reaction and 39.8 at% for a 6-hour reaction. Thus, as shown in figure 11a, the O/Al ratios are calculated to be 1.47, 1.44 and 1.47, respectively. The O/Al ratios do not reflect any relation with reaction times, although both concentrations of oxygen and aluminium have been increased slightly. This suggests that the O/Al ratios are independent of reaction times.

The carbon content at 105 °C is quantified to be 4.2 at% from a 1-hour reaction compared to 3.5 at% from a 3-hour reaction and 1.8 at% from a 6-hour reaction (Fig. 11b), showing less carbonaceous contaminations when the reaction occurs longer at the same temperature. This suggests that the β-elimination has been achieved within the reaction time and by-products are effectively removed. Thus, it can be concluded that the compositional quality of films has been improved at higher deposition temperatures (or pressures).
Figure 11. O/Al ratios (a) and carbon concentrations (b) of 
Al$_2$O$_3$ films prepared at various reaction times

4.5.2 Effects on the film morphology

Figure 12 shows the surface morphology of film that ran for a 1-hour 
experiment at 85 °C. Densely packed particle are observed with size ranging 
25 – 30 nm (Fig. 12a). Gaps (~5 nm in width) among particle grains are 
visible. This adhesive layer is 240 nm in average thickness (Fig. 12b).
A decrease in the particle size is observed from the surface morphologies of deposited films (Fig. 13a, 13c & 13e). The particle size ranges 31 – 57 nm (3-hour reaction), 26 – 32 nm (6-hours reaction) and 19 – 31 nm (12-hour reaction). Cross-section SEM images reveal adhesive films and random aggregation of deposited particles (Fig. 13b, 13d & 13f). The thickness of film deposited for 3 hours is less uniform than those deposited for 6 hours and 12 hours. The average film thicknesses vary from 240 nm (1-hour reaction), 300 nm (3-hour reaction), 210 nm (6-hour reaction) to 150 nm (12-hour reaction), indicating the independence of thickness to the reaction time. The results show that longer reaction time results in an increase in particle density, but a decrease in particle size.
Figure 13. SEM images of thin films deposited at 85 °C for various reaction hours: (a-b) 3 hours, (c-d) 6 hours, and (e-f) 12 hours.
4.6 Local co-ordination of Al and O

XRD experiments reveal amorphous structural integrity throughout the depth of prepared Al\(_2\)O\(_3\) thin films. Complementary short-range NEXAFS is used to study the evolution of local structure within the films. Figure 14 shows Al absorption spectra that are determined indirectly by measuring the drain current (see chapter 2). In figure 14a, two absorption peaks are obtained at 1567.2 eV and 1571.5 eV, respectively. They reveal the presence of a tetrahedral (AlO\(_4\)) co-ordination and an octahedral (AlO\(_6\)) co-ordination in the Al\(_2\)O\(_3\) reference.\(^9\) In figure 14b, an unresolved absorption peak appears at 1568 – 1570 eV, at which a strong Al absorption peak appears in polycrystalline \(\gamma/\theta\)-Al\(_2\)O\(_3\) reference.\(^{10}\) Two visible peaks are found at 1569.0 eV and 1571.5 eV, which are absorption peaks for AlO\(_6\) co-ordination,\(^9\) in film F105 (Fig. 14c). The observation on the increase of AlO\(_6\) at near 1569 eV indicates that the tenancy of AlO\(_4\) co-ordination evolves to AlO\(_6\) co-ordination at higher deposition temperature.

This co-ordination difference may be explained by the mechanism of the solvothermal reaction. The thermal decomposition that broke down the cluster of precursor occurs initially, so the Al-O fragments are released and the organic ligands separated. Then the Al-O fragments are precipitated, adsorbed and aggregated on the surface of the Si substrate. Films are grown along the c-axis. At 105 °C, the diffusion mechanism results in a dense population under extraordinary temperature and pressure, and thus its phase reconstructs to produce polycrystalline phases.
Figure 14. NEXAFS spectra showing the Al absorption peaks of (a) amorphous $\text{Al}_2\text{O}_3$ on the Al surface, (b) film F65 and (c) film F105.

Figure 15 shows the NEXAFS spectra of O absorptions for selected samples. A broad O absorption peak is observed at photon energies of 538 – 542 eV in figure 15a, indicating the native oxide layer on the surface of Al metal. The absorption peak at 541.6 eV appears to be relative intense than the shoulder-shape peak at 538.2 eV. Unresolved O absorption peaks are also detected near 538 eV and 542 eV in the spectrum of film F65 (Fig. 15b). There are no significant differences between the spectra of film F65 and film F105 (Fig. 15c). Thus, the evolution of O co-ordination depending on temperatures is not observed from the NEXAFS spectra of the films.
Figure 15. NEXAFS spectra showing the O absorption peaks of (a) amorphous Al₂O₃ on the Al surface, (b) film F65 and (c) film F105.
4.7 Summary and conclusion

Stoichiometric Al$_2$O$_3$ films were made using ADIC as a single-source precursor at temperatures <125 °C under solvothermal conditions. These films have low carbon concentration (minimum 1.8 at%). Surface morphology revealed densely packed particles that tended to decrease in size as the temperature increased. The quality of film deposited at higher temperatures exceeded that obtained at lower temperatures. Amorphous films were produced at temperatures below 100 °C. An octahedrally dominant Al absorption peak was found in the film prepared at 105 °C, suggesting a tendency for the long-range crystal growth.

SEM cross-section images revealed the as-deposited films had various thicknesses that were not dependent on reaction temperatures or reaction times. Both parameters controlled the compositional quality which was improved as the reaction temperature or the reaction time increased. Future work would investigate the factor that controls the deposition thickness.

4.8 References

Chapter 5

Syntheses and thermal properties of single-source aluminium carbamate precursors

5.1 Introduction

The selection of suitable precursors was based on identifying characteristic physicochemical feature that would allow efficient transport and clean decomposition (see chapter 1). As a result, conventional aluminium precursors range from inorganic,\textsuperscript{[1-3]} organometallic \textsuperscript{[4-6]} and metal organic compounds.\textsuperscript{[7-11]}

Previous work showed that metal dialkylcarbamates successfully prepared crystalline MgO and ZnO thin films via SSCVD,\textsuperscript{[12-17]} demonstrating the formation of crystalline thin films at a temperature 350 °C lower than using conventional precursor. This chapter describes the preparation of a chemical class of aluminium dialkylcarbamate precursors. The alkyl group includes ethyl, isopropyl, butyl and sec-butyl. Their thermal stabilities have been investigated for the use of chemical deposition in the vapour or liquid phase.
5.2 Experimental details

5.2.1 Aluminium diisopropylcarbamate

The synthesis of aluminium(III) diisopropylcarbamate (ADIC) is adapted from the literature method (Eq. 1).\[^{[18]}\]

\[
2\text{AlCl}_3 + 6\text{CO}_2 + 12\text{iPr}_2\text{NH} \rightarrow \text{Al}_2(\text{O}_2\text{CNR}_2)_6 + 6[\text{iPr}_2\text{NH}_2]\text{Cl} \quad (1)
\]

Schlenk techniques were employed, due to the moisture sensitivity of the product. Dry diisopropylamine (15.16 g, 0.150 mol) and benzene (100 ml) were stirred at room temperature, whilst CO\(_2\) gas was introduced in order to pre-saturate the mixture. AlCl\(_3\) (3.21 g, 0.024 mol) was then added, resulting in a gel-like mixture, which then becomes less cloudy and viscous after several hours of CO\(_2\) bubbling. The gas bubbling was stopped, whereupon some solid salts settle, and the clear supernatant solution was siphoned off and evaporated under vacuum. The solid residue was dried under vacuum at 80 °C to give a white powder of Al\(_2\)(O\(_2\)CNiPr\(_2\))\(_6\) (7.83 g, 71.0% yield), which was stored under N\(_2\). \(^1\text{H}\) NMR (DMSO, 25 °C), \(\delta\) ppm from TMS: 0.92. (doublet, \(J=0.018\), NCH(CH\(_3\))\(_2\)); 2.81 (septuplet, \(J=0.012\), NCH). \(^{13}\text{C}\) NMR (DMSO, 25 °C), \(\delta\) ppm from TMS: 23.1 (NCH(CH\(_3\))\(_2\)); 44.5 (NCH). Elemental analysis: C, 51.4; H, 9.12; N, 8.83; O, 15.0%, (Al\(_2\)C\(_4\)H\(_{32}\)N\(_6\)O\(_{12}\) requires C, 54.9; H, 9.21; N, 9.14%; O, 20.9%).

5.2.2 Aluminium diethylcarbamate

The synthesis of aluminium(III) diethylcarbamate (ADEC) follows the preparation of precursor ADIC. Dry diethylamine (12.0 g, 0.163 mol) and benzene (100 ml) were used. AlCl\(_3\) (3.39 g, 0.025 mol) was added. A pale
yellow powder of Al$_2$(O$_2$CNEt$_2$)$_6$ (0.59 g, 6.2 % yield) was produced. $^1$H NMR (DMSO, 25 °C), δ ppm from TMS: 1.11. (triplet, $J$=0.015, NCH$_2$CH$_3$); 2.77 (quartet, $J$=0.014, NC$H_2$). $^{13}$C NMR (DMSO, 25 °C), δ ppm from TMS: 12.1 (NCH$_2$CH$_3$); 41.8 (NCH$_2$); 128.5 (O$_2$CN). Elemental analysis: C, 41.0; H, 7.54; N, 8.57; O, 17.4%, (Al$_2$C$_{30}$H$_{60}$N$_6$O$_{12}$ requires C, 48.0; H, 8.05; N, 11.2; O, 25.6%).

5.2.3 Aluminium dibutylcarbamate

The synthesis of aluminium(III) dibutylcarbamate (ADBC) follows the preparation of precursor ADIC. Dry dibutylamine (13.7 g, 0.106 mol) and benzene (100 ml) were used. AlCl$_3$ (3.52 g, 0.026 mol) was added. A white powder of Al$_2$(O$_2$CNBu$_2$)$_6$ (7.45 g, 77.6 % yield) was produced. $^1$H NMR (DMSO, 25 °C), δ ppm from TMS: 1.42 (triplet, $J$=0.024, N(CH$_2$)$_3$CH$_3$); 1.95 (multiplet, $J$=0.020, NCH$_2$(CH$_2$)$_2$CH$_3$); 1.95 (triplet, $J$=0.019, NCH$_2$(CH$_2$)$_2$CH$_3$). $^{13}$C NMR (DMSO, 25 °C), δ ppm from TMS: 13.7 (N(CH$_2$)$_3$CH$_3$); 19.6 (N(CH$_2$)$_2$CH$_2$CH$_3$); 32.0 (NCH$_2$CH$_2$CH$_2$CH$_3$); 55.9 (NCH$_2$(CH$_2$)$_2$CH$_3$); 160.5 (O$_2$CN). Elemental analysis: C, 44.2; H, 9.37; N, 10.8; O, 12.8%, (Al$_2$C$_{54}$H$_{108}$N$_6$O$_{12}$ requires C, 59.6; H, 10.0; N, 7.73; O, 17.7%).

5.2.4 Aluminium di-sec-butylcarbamate

The synthesis of aluminium(III) di-sec-butylcarbamate (ADSC) follows the preparation of precursor ADIC. Dry di-sec-butylamine (13.6 g, 0.105 mol) and benzene (100 ml) were used. AlCl$_3$ (2.25 g, 0.017 mol) was added. A white powder of Al$_2$(O$_2$CN$_2$Bu$_2$)$_6$ (4.94 g, 53.9% yield) was produced. 1.35 (triplet, $J$=0.018, NCH$_2$CH($CH_3$)$_2$); 3.24 (doublet, $J$=0.019, NCH$_2$CH($CH_3$)$_2$). $^{13}$C NMR (DMSO,
25 °C), δ ppm from TMS: 9.6 and 15.2 (NCH2CH(CH3)2); 25.3 (NCH2CH(CH3)2); 51.4 (NCH2CH(CH3)2). Elemental analysis: C, 55.6; H, 10.4; N, 7.57; O, 16.8%, (Al2C54H108N6O12 requires C, 59.6; H, 10.0; N, 7.73; O, 17.7%).

Figure 1. Schematic structure of carbamate class precursors.

<table>
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</table>

5.2.5 TGA experiments

TGA was employed to study the thermal decomposition of aluminium dialkylcarbamate precursors on a Metter Toledo instrument. Each experiment proceeds at 1 atm under N2 atmosphere. A flow for sheath gas of N2 was set at 30 ml/min. The experiment investigates the thermal decomposition point of a precursor in a temperature range from 35 to 800 °C. An alumina crucible was heated at 5 °C/min from 35 °C to 300 °C, and then heated at 10 °C/min to 800 °C to ensure a complete decomposition of the precursor. Differential thermal analysis (DTA) experiments were also conducted to investigate the thermodynamic of a precursor during its decomposition.
5.3 Results

Aluminium dialkylcarbamate precursors were produced in a simple one-pot reaction (Eq. 2). The carbamate ion \([O_2CNR_2]\) was initially formed by pre-saturating a dialkylamine/benzene mixture with CO$_2$. Addition of AlCl$_3$ immediately resulted in a gel-like mixture, which presumably contained some polymeric intermediate. With continued stirring and bubbling with CO$_2$, the gel became less viscous, and eventually turned into a mixture of white granular precipitate suspended in a non-viscous clear supernatant. The white precipitate (dialkylammonium chloride) and unreacted AlCl$_3$ were allowed to settle, and the supernatant containing the carbamate was separated and evaporated to yield the product.

\[
2\text{AlCl}_3 + 6\text{CO}_2 + 12\text{R}_2\text{NH} \rightarrow \text{Al}_2(\text{O}_2\text{CNR}_2)_6 + 6[\text{R}_2\text{NH}_2]\text{Cl} \tag{2}
\]

where \(R = \) ethyl (CH$_2$CH$_3$); isopropyl (CH(CH$_3$)$_2$); butyl ((CH$_2$)$_3$CH$_3$); sec-butyl (CH$_2$CH(CH$_3$)$_2$).

During the synthesis of these precursors, it was observed that the difficulty to separate the supernatant from dialkylammonium chloride decreased when the ethyl was replaced by a larger alkyl group. The carbamate becomes more non-polar as the length of the carbon chain in the ligand increases. Thus the carbamate is more soluble in benzene. On the other hand, the polarity of dialkylammonium chloride has been affected less by the increase in the length of the carbon chain, as the ionic charge of ammonium dominates its polarity.

5.3.1 XPS characterisation of precursors

XPS was used to examine the metal organic compounds. All elemental compositions (except H) presented in a sample are determined. Figure 2 is a
typical XPS spectrum of ADIC. The peaks at binding energies of 531.5, 399.4, 285.0, 118.6 and 73.7 eV reflect the electrons emitted from the orbital of O 1s, N 1s, C 1s, Al 2s and Al 2p, respectively (Table 1). These emission peaks indicate the presence of components of O, N, C and Al in the precursor ADIC. The atomic ratio of C : N : O : Al in the precursor is calculated to be 8.0 : 1 : 2.4 : 0.6, which is close to the theoretical ratio 7 : 1 : 2 : 0.3 (42C : 6N : 12O : 2Al).

Figure 2. Survey scan XPS spectrum of precursor aluminium diisopropylcarbamate

<table>
<thead>
<tr>
<th></th>
<th>C 1s</th>
<th>N 1s</th>
<th>O 1s</th>
<th>Al 2p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Binding energy (eV)</td>
<td>531.5</td>
<td>399.4</td>
<td>285.0</td>
<td>73.7</td>
</tr>
<tr>
<td>Atomic ratio</td>
<td>8</td>
<td>1</td>
<td>2.4</td>
<td>0.6</td>
</tr>
</tbody>
</table>
In a high-resolution XPS scan, the chemical information such as chemical state and functional group can be obtained. Diisopropylcarbamate ligand contains three types of carbons: a quaternary carbon, a tertiary carbon and two primary carbons. Figure 4a reveals their presence at binding energies of 289.2, 286.1 and 284.9 eV, assigned respectively to the carboxyl carbon \( \text{O}_2\text{C} \), \( \alpha \)-carbon \( \text{NCH(CH}_3)_2 \) and \( \beta \)-carbon \( \text{NCH(CH}_3)_2 \) of the carbamate ligand (Fig. 2a). The measured atomic ratio of these carbon atoms is 1 : 2.5 : 4.6, which approximates the ratio expected for the precursor molecule (1 : 2 : 4).

Figure 4. High-resolution XPS spectra of Al\(_2\)(O\(_2\)CN\(_2\)Pr\(_2\))\(_6\) showing a) C 1s scan; b) N 1s scan; c) O 1s scan and d) Al 2p scan
The observed deficit of carboxyl C relative to α- and β-C reflects the presence of a small amount of diisopropylamine. This is confirmed from the N 1s spectrum (Fig. 4b), in which a major peak at 399.7 eV and a minor peak at 401.0 eV are attributed to the carbamate N and amine N, respectively. Figures 4c and 4d show the O 1s peak at 531.8 eV and the Al 2p peak at 74.4 eV. The symmetry of the O 1s peak suggests that only one type of O atom is present in ADIC. Its narrow peak width (FWHM = 1.7 eV) is also consistent with the presence of the single O. Any OH group due to partial hydrolysis impurities would appear at higher binding energies. Furthermore, the symmetrical O 1s peak indicates this compound is anhydrous.

5.3.2 Thermal properties of aluminium dialkylcarbamate precursors

$T_{\text{onset}}$ is the temperature at which a precursor begins to decompose. The value is measured at the exact point of deflection of mass loss. Since the precursor ADIC was relatively unstable at the beginning of heating due to its sensitivity to moisture or air, TGA shows a decreasing curve rather than a stable flat curve (Fig. 5). Thus, it is difficult to accurately measure $T_{\text{onset}}$. $T_0$, on the other hand, is more readily measured. $T_0$ is a point at which the loss rate of a chemical’s mass reaches maximum. $T_0$ of ADIC is measured as 109 °C.

At a temperature range between 50 – 150 °C, the decomposition of ADIC shows a single smooth curve, indicating that the thermal decomposition of ADIC is not proceeding in stages through intermediates of different stabilities. The decomposition of ADIC is complete at ~300 °C, resulting in a residue of 12.1 m%, which agrees with the formation of $\text{Al}_2\text{O}_3$ (theoretical value 11.1 m%). The DTA curve (pink curve) shows $T_c$ is below 0°C at the decomposition point 109 °C, indicating an endothermic reactions during the
decompositions of precursor ADIC, in which small molecules such as CO₂ would be released.

Figure 5. Thermal decomposition of aluminium diisopropylcarbamate

Figure 6. Thermal decomposition of aluminium diethylcarbamate
Furthermore, newly synthesised carbamate precursors ADEC, ADBC and ADSC have also been tested. Precursor ADBC experiences a single-step decomposition, as shown, indicating that only one $T_0$ is obtained at 126 °C. At temperatures $> 292$ °C, the decomposition of ADBC is close to completion. Its DTA curve shows an exothermic reaction ($T_c < 0$ °C at the deposition point 126 °C).

The decomposition pathway of precursors ADBC and ADSC experience multiple steps, as shown in figures 7 and 8. Three $T_0$ values are obtained at 55, 112 and 228 °C, respectively (Fig.7). $T_0$ at 55 °C is due to the loss of water. The major decomposition of ADBC occurs at 112 °C, as its mass has decreased to 2.8 mg from 7.3 mg. $T_c$ values at 55 and 112 °C are below 0 °C, indicating that both reactions are exothermic. The heat transfer at 228 °C is difficult to conclude, because the change of $T_c$ value is small at $T_c = 0$ °C. In figure 8, the TGA curve shows two decomposition reactions at 130 °C and 206 °C and both are exothermic reactions.

Figure 7. Thermal decomposition of aluminium dibutylcarbamate
Their $T_0$ values are compared and shown in table 2. The first decomposition points of carbamate precursors are all $\leq 130$ °C. In particular, precursor ADIC has the lowest temperature of 109 °C. ADBC and ADSC have a higher decomposition point than ADIC. This is due to their higher molecular mass. The higher decomposition point of ADEC cannot be explained by its molecular mass, since ADEC has the smallest molecular structure. However, the ethyl ligand has the shortest carbon chain, thus it is the least hindered structure. Therefore, the intermolecular force would be the reason for its higher decomposition point.
Table 2. Decomposition points of prepared aluminium dialkylcarbamate precursors.

<table>
<thead>
<tr>
<th>Precursors</th>
<th>First decomposition point (°C)</th>
<th>Second decomposition point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ADIC</td>
<td>109</td>
<td>–</td>
</tr>
<tr>
<td>ADEC</td>
<td>126</td>
<td>–</td>
</tr>
<tr>
<td>ADBC</td>
<td>112</td>
<td>228</td>
</tr>
<tr>
<td>ADSC</td>
<td>130</td>
<td>206</td>
</tr>
</tbody>
</table>

5.4 β-elimination mechanism for low-temperature decomposition

Using the same method, the $T_0$ are found for Al isopropoxide (Alisop), Al acetylacetonate (Alacac) and Al acetate (Alact) to be approximately 127 °C, 229 °C and at 262 °C, respectively. Alisop has the lowest decomposition point.

![Figure 9](image_url)

Figure 9. Structures of conventional aluminium precursors showing only Al isopropoxide contains β-hydrogen
The decomposition pathway of Alisop is proposed via a β-elimination mechanism,[19,20] due to its isopropyl ligand containing the β-hydrogen (Fig. 9). On the other hand, the structures of Alacac and Alact do not have a β-hydrogen, the decomposition cannot undergo β-elimination reaction and thus requires high temperatures. These results support the hypothesis that a β-elimination reaction would lower the decomposition point.

5.5 Summary and conclusion

The thermal characteristics of aluminium(III) dialkylcarbamate precursors were investigated with thermogravimetric analysis. Results indicated that precursors with β hydrogen decomposed at lower temperatures than those without. This finding allows us to propose a decomposition pathway via β-elimination that requires lower decomposition energy. Based on the hypothesis, we would be able to use carbamate precursors for solvent-free and solvent-based deposition methods at reduced temperatures.

5.6 References

Chapter 6

Low-temperature fabrications of polycrystalline $\text{Al}_2\text{O}_3$ thin films by sol-gel and hydrothermal reactions

6.1 Introduction

This chapter describes a new deposition strategy which is different from previous decomposition methods (see chapter 3 and 4) Instead of decomposing a precursor, this method synthesises polycrystalline $\text{Al}_2\text{O}_3$ thin films at a temperature as low as 200 °C via a urea hydrolysis reaction followed by a hydrothermal treatment.

Although aluminium oxide was formed in many shapes, such as spherical particles,[1] gel,[2] or powders,[3] via the urea hydrolysis reaction, thin film depositions have not been reported.

The important feature is the crystalline transformation of $\text{Al}_2\text{O}_3$ thin films via a hydrothermal treatment at elevated pressure. This approach produces crack-free films at temperatures as low as 200 °C—without conventional crystalline transformation by annealing.
6.2 Experimental details

6.2.1 Urea hydrolysis in water

Al(NO₃)₃•9H₂O (1.98 g, 5.27 mol) and urea (0.475 g, 7.90 mol) were weighed and dissolved in water (20 ml). The solution was heated in air. A Si <100> substrate was immersed in the hot solution for at least 1 hour. The now coated wafer was taken out and its edge pressed onto a filter paper to remove excess solution. The wafer was dried at 100 °C in air to remove water. The surface of the freshly prepared film exhibits optical band, probably due to the inhomogeneous coating. The resulting film is labelled as film w4, w6 or w8 (heated at 40, 60 or 80 °C, respectively).

6.2.2 Urea hydrolysis in glycerol

Al(NO₃)₃•9H₂O (1.98 g, 5.27 mol) and urea (0.475 g, 7.90 mol) were weighed and stirred in glycerol (20 ml). Although Al(NO₃)₃ was not soluble in viscous glycerol at room temperature, the solubility of nitrate increased at temperatures >40 °C. Al(NO₃)₃ was completely dissolved in the heated solution after 1 hour of stirring. A Si <100> substrate was immersed in the hot solution for minimum 2 hours. The coated Si wafer was spun 2 x 60 seconds at a speed of 1500 rpm by attaching its uncoated side onto the holding stage of a spinner, in order to remove excess glycerol. These films were then dried at 100 °C. They are labelled as film g4, g6 and g8 (in glycerol solvent at 40, 60 or 80 °C, respectively).
6.2.3 Hydrothermal reactions

The newly prepared Al hydroxide films, either from water or glycerol solutions, were hydrothermally treated. The sample was transferred into a Teflon® cell and water (500 μl) was added. The cell was placed in the reaction autoclave, which was subsequently heated at approximately 200 °C (pressure ~15.9 atm) for 24 hours. The reaction vessel was then slowly cooled to room temperature. The resulting film was dried at 100 °C for >1 hour to remove water and labelled as film w6h2 or g6h2.

6.3 Results and discussion

6.3.1 Chemistry of Al(OH)₃/Al₂O₃ formation

Equation 1 shows the hydrolysis of urea results in the production of hydroxide anions and by-products, including ammonium and hydrogen carbonate.[4] The subsequent reaction of hydroxide anions with Al cations produces Al(OH)₃ precipitate in the solution (Eq. 2). The hydroxide film deposited on the Si substrate is dehydroxylated, followed by hydrothermal treatment for the formation of polycrystalline Al₂O₃ thin films (Eq.3).

Urea hydrolysis:

\[ \text{NH}_2\text{C}(=\text{O})\text{NH}_2 \text{ (urea)} + 4\text{H}_2\text{O} \rightarrow 2\text{OH}^- + 2\text{NH}_4^+ + \text{H}_2\text{CO}_3 \]  

(1)

Hydroxylation:

\[ \text{Al}^{3+} + 3\text{OH}^- \rightarrow \text{Al(OH)}_3 \]  

(2)

Dehydroxylation:

\[ \text{Al(OH)}_3 \rightarrow \text{Al}_2\text{O}_3 \]  

(3)
6.3.2 XPS measurements

Figure 1a shows the wide scan XPS of the film w6. The main peaks at binding energies of 532.5 eV and 74.7 eV are attributed to the O 1s and Al 2p photoelectrons, respectively (assuming the binding energy of the adventitious C 1s photoelectrons is 285.0 eV). The peaks at binding energies of 400.2 eV and 407.1 eV are due to the N 1s photoelectrons in NH$_4^+$ and NO$_3^-$ groups, respectively. Quantification analysis shows a small concentration of the N (1.4 at%) and a high C impurity (43.9 at%) in the film. A small quantity of Si is also detected (2.4 at%) as the peaks of Si 2s and Si 2p photoelectrons are observed at 153.0 and 101.6 eV, respectively.

After Ar$^+$ etching treatments, the N and C concentrations are substantially reduced to 0.6 and 0.4 at%, respectively (Fig. 1b). This indicates both impurities are mainly restricted to the outer surface of the film. The Si 2s and 2p signals disappeared after etching. The initial detection of Si is probably due to the Si residue on the film surface when cleaving the sample for XPS measurements. The O 1s peak shifts to 531.6 eV while the Al 2p peak remains at 74.7 eV. The O-Al separation between binding energies of O 1s and Al 2p photoelectrons is 456.9 eV, suggesting that the film w6 consists of both O$^{2-}$ and OH$^-$.\cite{5,6} The presence of Al hydroxide is typically formed by hydration when exposing a surface to the air. The atomic ratio of O/Al after etching drops from 3.6, of a hydrated hydroxide to 1.4, of a near-stoichiometrical Al$_2$O$_3$. 
Figure 1. Survey scan XPS spectra of Al₂O₃ thin film deposited via urea hydrolysis before (a) and after (b) Ar⁺ treatment

Hydrothermal treatment of the hydroxylated films is carried out at 200 °C. In the XPS spectrum of the outer surface of the film w6h2 (Fig. 1b), the binding energies of O 1s and Al 2p photoelectrons are detected at 531.9 eV and 74.2 eV, respectively. After Ar⁺ etching, the O 1s peak shifts to 530.7 eV. The binding energy separation between O 1s and Al 2p peaks is 456.5 eV, suggesting the presence of major O²⁻ in the film w6h2.[5] This observation is mainly due to the dehydroxylation during the hydrothermal treatment. The concentration of the C impurity is 18 at% on the outer surface of the film and has decreased to 1.3 at% after etching.
In comparison, film w6a4 is obtained by annealing film w6 at ~400 °C in air. In film w6a4, the O 1s and Al 2p peaks are measured at binding energies of 531.8 eV and 74.2 eV, respectively. The O/Al ratio is calculated to be 1.3. The binding energy separation between O 1s and Al 2p peaks is 456.4 eV. A small Na 1s peak is visible at a binding energy of 1072.4 eV (concentration 0.7 at%). The carbonaceous content is 20.2 at%. After etching, both Na and C impurities are removed.

The results of the O/Al atomic ratios and O-Al separation of the hydrothermal and annealed films are listed in table 1. They show that both thermal treatment (w6a4) and hydrothermal treatment (w6h2) result in small O/Al ratios and energy separation. These films, particularly film w6h2, are oxygen deficient than stoichiometric Al₂O₃. These results are due to the dehydroxylation of hydroxides during thermal or hydrothermal treatment. Excessive hydroxides have been removed and resulted in a low O/Al ratio.

Table 1. O/Al ratios and O-Al separation between O 1s and Al 2p peaks measured before and after Ar⁺ treatment.

<table>
<thead>
<tr>
<th>Films</th>
<th>w6</th>
<th>w6a4</th>
<th>w6h2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O/Al ratio</td>
<td>O-Al separation</td>
<td>O/Al ratio</td>
</tr>
<tr>
<td>Outer surface</td>
<td>3.6</td>
<td>457.8</td>
<td>1.4</td>
</tr>
<tr>
<td>Etched surface</td>
<td>1.4</td>
<td>456.9</td>
<td>1.3</td>
</tr>
</tbody>
</table>
6.3.3 High-resolution XPS of hydroxide/oxide composition

A high-resolution region scan XPS spectrum of the O 1s peak in film w6 shows a shoulder at higher binding energy site (Fig. 2a). The fitted curve contains two peaks at 531.1 eV and 532.4 eV attributed to the O²⁻ and OH⁻, respectively.[5] This confirms the presence of a mixture of hydroxide/oxide in film w6. In addition, the intensity of the O²⁻ peak is greater than that of the OH⁻ peak, indicating the major product is O²⁻ by the thermal treatment.

Similarly, a region scan XPS spectrum of the hydrothermally treated film w6h2 shows the presence of hydroxide and oxide (Fig. 2b). This is also due to incomplete dehydroxylation of the hydroxide form during the hydrothermal treatment. The O 1s photoelectron of water (binding energy 533.5 – 533.7 eV [5]) is not detected in either film w6 or film w6h2. The absence of water suggests that the residual water is not incorporated in the film.

![Figure 2. High-resolution XPS region scans revealing the presence of O²⁻ and OH⁻ in the film w6 (a) and hydrothermally treated film w6h2 (b), respectively.](image)

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6.3.4 Film morphology

The SEM image of the dehydrated film w6 shows micro-cracking occurred across the surface of the prepared film (Fig. 3a). The formation of cracks is a result of thermal expansion during drying. The SEM image of the cross section shows the average film thickness to be 575 nm (Fig. 3b). It also appears that the film is partially adhered to the substrate and several fragile sections separate from the substrate. This appearance is due to the solution shrinkage during the drying process. The solvent existing on the outer surface evaporates faster than that in the bulk, leading to rapid shrinkage of the outer surface and a cracking formation.

Figure 3. Surface morphology and cross section view of film w6.

The surface morphology and cross section view of the film w6a4 annealed at 400 °C are shown in figure 4. Heating results in an increased density of many smaller cracks across the surface (Fig. 4a), which can be due to difference in heating rates. The heating rate of the film attached to Si is
faster than that of the unattached films. As a result, unattached Al₂O₃ tends to be more fragile and unstable on the surface of the substrate. Thus, the temperature difference causes cracking of the entire film. This shows that the conventional annealing treatment is not a suitable method for producing an adhesive coating on the Si substrate. The average thickness of the annealed film is measured to be 334 nm (Fig. 4b).

Figure 4. Surface morphology and cross section view of film w6a4 after thermal treatment at 400 °C.

Figure 5a shows the surface morphology of film w6h2 after hydrothermal treatment. A crack-free and uniform layer across the substrate surface is observed. The cross section SEM image (Fig. 5b) shows the average thickness of the film is ~461 nm. The film is well adhered onto the substrate and densely packed. Under high-pressure conditions, the particles are diffused uniformly to avoid further cracking and to produce a homogenous layer.
6.3.5 Film crystallographic structure

The XRD measurement of the dehydrated film w6 shows a strong Si $<200>$ diffraction at $2\theta = 33.2^\circ$, attributed to the underlying Si substrate (Fig. 6a). Several smaller diffraction peaks at $2\theta = 29.5$, 43.3, 47.7 and 48.7 are also detected. They are denoted to polycrystalline $\alpha$-$\text{Al}_2\text{O}_3$ (JCPDS10-173) and $\gamma$-$\text{AlOOH}$ (JCPDS21-1307). The presence of $\gamma$-$\text{AlOOH}$ in film w6h2 is in agreement with the XPS results above. After hydrothermal treatment, the diffraction intensity of these peaks enhanced substantially relative to that of the Si peak (Fig. 6b), suggesting a significant improvement in the crystallinity of the film.

It has been reported that the formation of $\alpha$-$\text{Al}_2\text{O}_3$ phase occurs at a temperature $>$1000 °C.\textsuperscript{[7]} In this case, the appearance of $\alpha$-$\text{Al}_2\text{O}_3$ phase involves a much lower temperature condition (i.e. $\sim$200 °C). In addition, a dominantly intensive reflection at $2\theta = 29.5$ and reflections at $2\theta = 47.7$ and
23.2 are not identifiable to any crystalline aluminium oxides or hydroxides references.

Figure 6. XRD diffraction patterns of (a) film w6 after drying at 100 °C and (b) the polycrystalline film w6h2 (● denotes α-Al₂O₃, ▼ denotes γ-AlOOH) after hydrothermal reaction at 200 °C.
6.3.6 Discussion of the film deposition mechanism

Shaw and Bordeaux showed the decomposition of urea produced cyanate and ammonium ion. The hydrolysis of urea in water produces hydroxide anions. OH⁻ anions then react with Al³⁺ cations to give Al(OH)₃. Decomposition of urea results in gaseous by-products CO₂ and NH₃. In this work, the formation of Al₂O₃ thin film is illustrated in a three-step process (Fig. 7).

Firstly, Al(OH)₃ particles are produced (Eq. 1 & 2) and slowly precipitate onto the surface of the substrate. The evaporation of water during the drying process increases the precipitation rate. As a result, a solid-state layer of Al(OH)₃ is formed. The solution containing soluble particles such as NH₄⁺, CO₃²⁻ and NO₃⁻ separates from this solid layer. Unstable ions such as NH₄⁺ and CO₃²⁻ are decomposed to give gaseous NH₃ and CO₂. When the water is completely evaporated, nitrate and carbonate residues remain on the outer surface of the thin film. This was confirmed by the XPS results, which show high carbonaceous and nitrogen concentrations present in the outer surface of film w6.

Secondly, continuous thermal condensation leads to high tensile stress that results in the formation of cracks. In the last step, the cracked film is treated under the hydrothermal condition. This significantly increases the diffusion of Al₂O₃ particles across the substrate surface. The diffusion simultaneously results in a densely packed film, as well as the growth of crystalline phases.
Figure 7. Schematic showing a three-step process for the formation of Al$_2$O$_3$/AlOOH thin film. (a) the solution deposition of Al hydroxide film by thermal dehydration; (b) the formation of cracks in the film during thermal condensation; (c) particle diffusion under hydrothermal conditions resulted in a crack-free and densely packed polycrystalline thin film.

6.4 Fabrication of thin films in glycerol

6.4.1 Film composition

Figures 8a – 8c show the wide scan XPS spectra of the hydrated film (g6), thermally treated film (g6a4) and hydrothermally treated film (g6h2). The inset shows the part of the scans after Ar$^+$ etching treatment. The O 1s and Al 2p photoelectron peaks in the spectrum of the film g6 are measured at binding energies of 530.9 eV and 73.8 eV, respectively (Fig. 8a). The spectrum also shows the concentration of N and C impurities to be 2.6 at% and 6.5 at%, respectively. Both impurities have significant concentrations on the outer surface. The inset of Fig. 8a shows relatively strong N 1s signals attributed to NH$_4^+$ (BE 400.2 eV) and NO$_3^-$ (BE 407.1 eV). The total N surface concentration was 4.7 at%. Surface carbonaceous impurity was also measured at ~49.0 at%. Although both N and C impurities are mostly removed, the results suggest that the bulk film contains N and C impurities
along the depth. The O/Al atomic ratio in the bulk has decreased from 3.4 to 1.3.

Figure 8. Survey scan XPS spectra of a) film g6 deposited at 60 °C in glycerol, b) by thermal treatment and (c) by hydrothermal treatment. Insets represent the spectra of the films before Ar⁺ etching.
Film g6a4 was produced by thermally annealing film g6 at 400 °C. In the spectrum of the bulk film (Fig. 8b), the O 1s and Al 2p peaks are measured at binding energies of 531.5 and 74.6 eV, respectively. Nitrogen residues are not detected in either the film or its outer surface (inset of Fig. 8b). The surface carbonaceous content is 9.3 at%, reduced to as low as 1.9 at% after etching (Fig. 8b).

Hydrothermal treatment was carried out at 200 °C. Figure 8c shows the O 1s and Al 2p peaks at binding energies of 530.0 and 73.6 eV, respectively. Nitrogen residue is not detected and carbon impurity concentration is measured at 4.8 at%. The nitrogen and carbon contents were 1.1 at% and 36.1 at%, respectively, on the outer surface (inset of Fig. 8c).

The O/Al atomic ratios and O-Al separation of the films after different treatments are listed in table 2. As above, the results show that both thermal treatment and hydrothermal treatment result in smaller O/Al ratio and O-Al separation. This also indicates an increase in O$^{2-}$ content, due to the hydroxide–oxide conversion.

Table 2. O/Al ratios and O-Al binding energy separations found on surfaces of films g6, g6a4 and g6h2 before and after Ar$^+$ treatment

<table>
<thead>
<tr>
<th>Films</th>
<th>g6</th>
<th>g6a4</th>
<th>g6h2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>O/Al ratio</td>
<td>O-Al separation</td>
<td>O/Al ratio</td>
</tr>
<tr>
<td>Outer surface</td>
<td>3.4</td>
<td>458.1</td>
<td>1.3</td>
</tr>
<tr>
<td>Etched surface</td>
<td>1.3</td>
<td>457.1</td>
<td>1.1</td>
</tr>
</tbody>
</table>
6.4.2 Film surface morphology

The surface morphology of film g6 is characterised with SEM. Compared to the film obtained in the aqueous solution, the surface of film g6 appears to have no micro-cracks. Instead, circular pores with a diameter ranging from 120 – 180 nm are visible on the surface of the film (Fig. 9a). A cross-section image shows a uniform layer with an average thickness of 191 nm (Fig. 9b). This layer appears to be a dense structure and no cracks are observable.

Figure 9. Surface morphology (a) and cross-section view (b) of film g6 prepared in glycerol at 60 °C.

Figures 10a and 10b show the film after thermal treatment at 400 °C. Surface cracks become clearly visible due to thermal expansion. The average film thickness is 338 nm. In comparison, figures 10c and 10d show that the hydrothermally treated film displays micro grains unevenly distributed on the surface of the substrate. However, there are no cracks formed in the film.
Figure 10. SEM images showing the surface and cross-section views of (a-b) film g6a4 thermally treated at 400 °C and (c-d) film g6h2 hydrothermally treated at 200 °C

6.5 Use of other Al ion sources

AlCl$_3$ or Al$_2$(SO$_4$)$_3$ are commonly used as aluminium precursors that generate Al$^{3+}$ in an aqueous solution. They were tested under the same condition as using nitrate. However, fabrication using Al$_2$(SO$_4$)$_3$ or AlCl$_3$ was unsuccessful. After several hours’ reaction, the solution did not adhere to the surface of the Si wafer. This is due to higher surface tensions of sulphate
and chloride solutions. The aqueous products are \( \text{NH}_4\text{NO}_3 \), \( \text{(NH}_4\text{)}_2\text{SO}_4 \) and \( \text{NH}_4\text{Cl} \), respectively, from urea hydrolysis reaction with different aluminium salts. Dutcher et. al \[9\] indicates that the linear surface tension coefficient (\( \text{d} \sigma/\text{d}m \), unit=\( \text{mN} \cdot \text{m}^{-1} \cdot \text{kg} \cdot \text{mol}^{-1} \)), which can be used to estimate the surface tension at low concentrations, for \( \text{NH}_4\text{NO}_3 \) is 0.95, whereas \( \text{d} \sigma/\text{d}m \) for \( \text{(NH}_4\text{)}_2\text{SO}_4 \) is 2.38 and for \( \text{NH}_4\text{Cl} \) is 1.19. It shows that sulphate and chloride solutions with higher surface tensions are less adhesive than nitrate solution.

**6.6 Summary and conclusion**

In this chapter, a novel approach combining sol-gel and hydrothermal treatment has been successfully developed for the formation of crystalline aluminium oxide thin films at a remarkably low temperature of 200 °C. The as-deposited films contained low carbonaceous impurities (< 3 at%), but were oxygen deficient (an O/Al ratio of 1.1) after either annealing or hydrothermal treatment. The results indicate that the dehydroxylation removed excessive hydroxide, and thus resulted in a lower O/Al ratio than stoichiometric \( \text{Al}_2\text{O}_3 \). Future studies are needed to investigate the mechanism behind the dehydroxylation during thermal or hydrothermal reactions.

A hydrated film was formed via urea hydrolysis at a temperature of 60 °C. Subsequent hydrothermal reactions converted the hydroxide to oxide films and promoted the formation of polycrystalline structures. Additionally, the polycrystalline films appeared to have crack-free surface morphology, demonstrating improved surface morphology and adhesion to the substrate than conventional annealing treatment. In particular, the film (461 nm thick) deposited in water showed densely packed and uniform morphology,
comparing to the appearance of micro grains in the film (338 nm thick) deposited in glycerol.

This low-temperature approach could be very useful for preparing polycrystalline Al₂O₃ thin films on a wide range of substrates. Future work will explore the crystal evolution under hydrothermal conditions and the deposition of Al₂O₃ thin films on various substrates with low melting points.

6.7 References

Chapter 7

Summary

A study into the deposition of aluminium oxide thin films by a series of different deposition techniques has been undertaken. There were a number of key interesting findings through the development of new concepts in the precursor chemistry.

In Chapter 1, the structures of metastable γ, δ, θ-Al₂O₃, and the stable α-Al₂O₃, together with their transformation temperatures have been discussed. A number of applications using Al₂O₃ thin films are based on the chemical and structural properties of the material. Additionally, a series of low-temperature depositions has been reviewed. Carbamate cluster complexes were highlighted as potential precursors which were competitive to conventional alkoxide and acetylacetonate precursors. Alternative low-temperature deposition method such as sol-gel depositions and hydrothermal reaction were also introduced.

Chapter 2 offered the project a number of experimental techniques. The techniques were employed in wide terms for the synthesis and characterisation of either precursors or thin films.
In Chapter 3 and Chapter 4, two comparative film growth techniques were made using the same novel, high nuclearity precursor—aluminium diisopropylcarbamate. A SSCVD technique produced high quality films and resulted in an orientated α <1 1 3> Al₂O₃ film at 550 °C. On the other hand, a solvothermal method achieved remarkably low deposition temperature (65 °C) to deposit amorphous Al₂O₃ thin films. Precursor chemistry was shown to be a driving force in these exciting results. A β-elimination mechanism for the decomposition of the carbamate complex was proposed to lead such low-temperature deposition.

The development of carbamates was outlined in Chapter 5. By devising a simple synthetic pathway, aluminium carbamate complexes were synthesised. Thermal analysis results showed that carbamate precursors containing β hydrogen decomposed at lower temperatures than those without. Based on the proposed β-elimination mechanism, these results provided information to improve SSCVD and solvothermal precursors that would require lower decomposition temperatures.

In Chapter 6, combined sol-gel and hydrothermal reactions have been successfully developed for the formation of polycrystalline Al₂O₃ thin films at a significantly low temperature (200 °C). A hydrated film was produced via urea hydrolysis at temperature 60 °C. A subsequent hydrothermal reaction converted the hydroxide to oxide films and promoted the formation of polycrystalline structures. This low-temperature approach could be very useful for preparing polycrystalline Al₂O₃ thin films on a wide range of substrates.
Single-source chemical vapor deposition of clean oriented Al$_2$O$_3$ thin films

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Clean oriented Al$_2$O$_3$ thin film with a dominant Al$_2$O$_3$ $<$1 1 3$> plane was deposited on Si $<$1 0 0$> substrate at 550 °C, by single-source chemical vapor deposition (CVD) using aluminium(III) diisopropylcarbamate, Al$_2$(O$_2$CN$i$Pr$_2$)$_6$. This process represents a substantial reduction in typical CVD film growth temperatures which are typically $>$1000 °C. Through the studies of thermal stability of this precursor, we propose a specific $|$-elimination decomposition pathway to account for the low temperature of the precursor decomposition at the substrate, and for the lack of carbon impurity byproducts in the resulting alumina films that are characterized using X-ray photoelectron spectroscopy and depth profiling.

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1. Introduction

Mechanically hard alumina thin films have been used widely in protective coatings [12]. The relatively high dielectric constant of alumina also makes its films suitable as the dielectric layer in metal oxide semiconductor field effect transistors [3,4]. Conventional chemical vapor deposition (CVD) method has produced alumina films utilizing a gaseous mixture of AlCl$_3$/H$_2$/CO$_2$ [5]. However, inherent disadvantages of using such precursor mixtures include a requirement to carefully control relative concentration of reagent gases, and handling the resulting corrosive HCl and toxic CO byproduct gases. Alternatively, metal-organic precursors including aluminium trialkyl [2,6], aluminium alkoxide [7–9], aluminium acetylacetonate [10–12] and aluminium tris–dipivaloylmethanate [13] have been applied to film deposition. Such depositions required additional oxygen sources from nitrous oxide or water vapor, which again required concentration control. Films made from these precursors were amorphous at the deposition temperatures of 600 °C.

Single-source (SS) CVD is a relatively simple approach that avoids using multiple sources by incorporating all necessary constituents within one molecule. Ideally, the precursor should be a solid with low temperature volatility, and a somewhat higher decomposition temperature, together with a clean decomposition pathway to deposit uncontaminated films.

Carbamates are a suitable class of compound for SS CVD, as they are known to undergo low temperature decomposition under reduced pressure, to produce volatile isocyanate and alcohol fragments that are readily removed [14]. We have previously prepared pure polycrystalline MgO thin films using magnesium diethylcarbamate as a SS precursor [15]. This was achieved at 450 °C — a much lower decomposition temperature than using the conventional precursor, magnesium tert-butoxide (800 °C) [16]. In our present work, aluminium(III) diisopropylcarbamate is employed as a SS precursor, for application to the deposition of Al$_2$O$_3$ thin films. The core of this molecule contains an Al atom coordinated octahedrally with six O atoms. Notably, this coordination is similar to the AlO$_6$ coordination in hexagonal close-packed α-Al$_2$O$_3$, and it may provide some preorganization to aid oxide deposition.

2. Experimental details

2.1. Preparation of the SS precursor — Al$_2$(O$_2$CN$i$Pr$_2$)$_6$ (1)

Aluminium(III) diisopropylcarbamate Al$_2$(O$_2$CN$i$Pr$_2$)$_6$ was produced in a simple one-pot reaction [17]. Schlenk techniques were employed, due to the high sensitivity of the product to moisture. The carbamate ion [O$_2$CN$i$Pr$_2$]$^-$ was initially formed by pre-saturating a mixture of diisopropylamine (15.16 g, 0.150 mol) and benzene (100 ml) with CO$_2$ bubbling. Addition of AlCl$_3$ (3.21 g, 0.024 mol) immediately resulted in a gel-like mixture, which presumably contained some polymeric intermediate. With continued stirring and bubbling with CO$_2$, the gel became less viscous, and eventually turned into a mixture of white granular precipitate suspended in a mobile clear supernatant solution. The white
precipitate containing alkylammonium chloride and unreacted AlCl₃ was allowed to settle, and the supernatant containing the product was separated and evaporated to yield a white powder of Al₂(O₂CNiPr₂)₆ (1) (7.83 g, 71.0% yield), which was stored under N₂. H¹ nuclear magnetic resonance (CDCl₃): δ ppm, 1.15 (doublet, J = 0.02); 3.86 (septuplet, J = 0.02). Elemental analysis: C, 51.4; H, 9.12; N, 8.83%. (Al₂C₄₂H₈₄N₆O₁₂ requires C, 54.9; H, 9.21; N, 9.14% and reported C, 53.0; H, 8.9; N, 8.4% [17]).

2.2. CVD of Al₂O₃ thin films

The film deposition was carried out in a low pressure CVD chamber with a constant background pressure of ~1.33 × 10⁻⁴ Pa. Silicon <1 0 0> wafer was ultrasonicated sequentially in diluted hydrochloric acid, demineralized water, then acetone, for 10 min each, prior to loading into the deposition chamber. Carbamate precursor 1 was loaded into a Knüdsen cell. During film growth, the Knüdsen cell was heated slowly to approx. 150 °C in order to sublime the precursor gradually, whilst the Si substrate temperature was maintained at a temperature range of 450 °C to 550 °C, for the various experiment runs.

2.3. Instrumentation

Thermogravimetric analysis (TGA) was carried out in Perkin Elmer Pyris 1 TGA. The sample (~10 mg) was heated under N₂ gas at 2 °C/min from 25 °C to 300 °C, and then 5 °C/min up to 850 °C to ensure a complete decomposition or oxidation. A flow for sheath gas was set at 20~35 ml/min at 1.38~2.41 × 10⁴ Pa and for balance purge at 2.76~4.14 × 10⁵ Pa. X-ray photoelectron spectroscopy (XPS) spectra were obtained using a VG ESCALAB 220i-XL spectrometer equipped with a monochromate Al Kα X-ray source which emitted a photon energy of 1486.6 eV at 10 kV and 12 mA. The measures were processed at a step size either 1 eV (wide scans) or 0.1 eV (region scans). Film samples were screwed down to Al holders. Precursor samples were adhered to the surface of In metal and then mounted on Al holder. Samples were measured in the analysis chamber at a typical operating pressure of approx. 1.33 × 10⁻⁷ Pa and 2.66 × 10⁻⁵ Pa during Ar ions etching. The Ar ion gun filament delivered a sputtering rate of approx. ~2 Å/sec. An electron flood gun was used to reduce the charging effect. Curve fitting and quantification of XPS spectra were performed using Eclipse and CasaXPS programs. X-ray diffraction (XRD) measurements of the films were carried out using Philips X’pert MRD. Cu X-ray generator was operated at 45 kV and 40 mA and supplied a Kα emission with a wavelength of 1.5418 Å. Films were scanned for 2θ axis only at a step size of 0.05 2θ in a continuous scan mode. The morphology and microstructure of the films were determined using a Hitachi s900 scanning electron microscope (SEM) instrument. Al₂O₃ film samples were sputter coated with chromium to enhance conductivity for acquiring images. High-resolution SEM images were obtained at a magnification of x100 k and at an operational voltage of 4 kV.

3. Results and discussion

Fig. 1 shows the XPS region scans of precursor 1 (the wide scan XPS spectrum of this precursor is shown in Fig. 4 for comparison with that of deposited films). The C 1s spectrum reveals three component peaks at binding energies of 289.2, 286.1 and 284.9 eV, assigned respectively to the carboxyl carbon (O₂CN), α-carbon (NCH(CH₃)₂) and β-carbon (NCH(CH₃)₂) of the carbamate ligand (Fig. 1a). The measured ratio of these carbon atoms is 1:2.5:4.6, which approximates the ratio expected for the precursor molecule (1:2:4). The observed deficit of carboxyl C relative to α- and β-C may reflect the presence of a small amount of diisopropylamine contamination. This is confirmed from the N 1s spectrum (Fig. 1b), in which a major peak at 399.7 eV and a minor peak at 401.0 eV are attributed to the carbamate N and amine impurity N, respectively. Figs. 1c and d show the O 1s peak at 531.8 eV and the Al 2p peak at 74.4 eV. The observed symmetry of the O 1s peak suggests that only one type of O atom is present in 1. Any hydroxyl...
groups due to partial hydrolysis impurities would appear at higher binding energies. Furthermore, the symmetrical O 1s peak indicates this compound is anhydrous. The atomic ratio of C:N:O:Al from these XPS spectra is estimated as 8.0:1:2.4:0.6.

TGA was employed to study the thermal stability of carbamate 1. Sublimation of 1 occurred at a temperature range from 50 °C to ~156 °C and is shown as a rapid weight loss (Fig. 2). This single step also indicates that the sublimation of 1 was not proceeding any evaporation of solvate. Following decomposition is observable at above 156 °C and results a residue (aluminium oxide) of 12.1 mass% of the original precursor. The sublimation point of 1 is estimated to be 70 °C which is the weight loss onset temperature (Tonset) [18]. Using the same method, we found that Tonset for aluminium triisopropoxide (Aldrich) is approx. 98 °C and Tonset for aluminium acetylacetonate (Lancaster) is approx. 188 °C. Carbamate 1 thus has the lowest sublimation temperature of the three tested alumina precursors. The low volatility of 1 can be explained at molecular level. In the core of aluminium(III) diisopropylcarbamate, each Al atom is coordinated octahedrally by six donor O atoms (Fig. 3 inset). The diisopropyl groups surround the core of this complex, so intermolecular polar bonding is inhibited. This structural feature, together with the compact globular form of the dimeric complex, should lower the intermolecular forces, thus accounting for the significant volatility of 1 under high vacuum.

Furthermore, a clean decomposition pathway counts additional suitability to a quality precursor. Like most metal-organic CVD, pyrolysis of 1 is the key reaction in film’s deposition. This thermal reaction is dependent on the precursor’s molecular structure and its decomposition temperature. From previous studies on the pyrolysis of carbamates and their derivatives [14,19]. Dyer et al. found that the thermal decomposition of some carbamate compounds occurred at 200 °C under reduced pressure, and they isolated isocyanate and alcohol fragments [14]. On the basis of these studies, the proposed mechanism for the thermal decomposition of carbamate 1 is illustrated in Fig. 3. The small, highly charged Al³⁺ should polarize the attached carbamate ligand, thereby promoting its fragmentation by loss of oxide ions. It is envisaged that the N lone pair and the β hydrogen atom would participate in a β-elimination reaction. This route would produce an alkyl isocyanate and propene as fragments. Both byproducts are highly volatile under vacuum, thus they would be evaporated immediately after decomposition and clean alumina composition will be expected to be obtained. Al–O compositional sufficiency, low volatility of 1 and clean decomposition pathway indicates carbamate 1 is an appropriate candidate to SS CVD.

Films made from 1 at various substrate temperatures were characterized by XPS. Surface analysis and depth profiling reveal the composition, on the surface and throughout the depth, of the films. We found that no film deposited on a Si<100> substrate at 450 °C, as no Al peaks are observable in the XPS spectrum. At higher substrate temperatures of 500 °C and 550 °C, both Si wafers become coated with shiny blue films, whose surface XPS spectra and depth profilings show insignificant differences. Fig. 4 compares the wide scan XPS spectra of 1 (Fig. 4a) and of the film grown from it at 550 °C (Fig. 4b). Of significance is the disappearance of the N 1s peak at binding energy...
of near 400 eV in the spectrum of the film, indicating a comprehensive decomposition of precursor. A C 1s peak is still visible in the film at binding energy of 285.2 eV, though its intensity has reduced substantially comparing to that in precursor. This C was removed after an argon ion sputtering treatment (Fig. 4c) and its remaining became a negligible amount (~1 atomic percent (at.%)), suggesting this C impurity is primarily on the film surface. The O:Al atomic ratio is to be 1.37, in agreement with a previous analysis of Al2O3 films [20].

Depth profiling examines that the O and Al concentrations of the film deposited at 550 °C (Fig. 5) remain constant at approx. 58 at.% and 42 at.% (atomic ratio of O to Al ≈ 3:2) throughout the depth of the film. The purity and uniformity of deposited films suggest Al(III) diisopropylcarbamate fulfills the demand for Al2O3 film growth via SS CVD.

Fig. 6 represents XRD patterns of Si wafer and the films grown at different substrate temperatures. In blank Si, a strong peak appears at 69.1 2θ due to the diffraction by single crystal Si <1 0 0> (Fig. 6a). No diffraction pattern of crystalline Al2O3 structure is detected for the film made at 500 °C (Fig. 6b), which indicates the film is amorphous. The diffraction pattern of Al2O3 film grown at 550 °C shows the Si <1 0 0> peak and an additional peak at 43.6 2θ (Fig. 6c). This prominent peak attributed to the formation of oriented Al2O3 <1 1 3> phase. This crystallite orientation is found in α-Al2O3 [21] formed by conventional CVD at a substrate temperature higher than 1000 °C [22,23]. In comparison with the 550 °C film, the amorphous alumina film deposited at 500 °C was post-annealed at approx. 850 °C for 2 h in air. Its diffraction pattern then showed the formation of a different Al2O3 crystalline phase – along the <4 0 0> direction (45.9 2θ) – as shown in the inset of Fig. 6b. This crystalline phase is also observed in metastable δ-Al2O3 which is typically obtained from annealing boehmite at temperatures above 800 °C [24,25].

Since the [0 0 1] phases have lowest surface free energy, the planes along c-axis would be formed prior to other orientations. Thus under thermally activated condition, i.e. annealing, the <4 0 0> plane has been grown first. During annealing treatment, diffusion of atoms, removal of crystal defects and recrystallization attribute to polycrystalline formation at excessively high temperature. The dehydration of hydroxyl on the film’s surface as well as oxidation of impurities may also raise annealing temperature. In contrast, the growth of the <1 1 3>-plan suggests a different growth mechanism on the surface of Si.
substrate. With pre-organized octahedral Al—O core, this plane has been made at a temperature of 550 °C. Further studies using Synchrotron X-ray absorption techniques will assist the understanding of atomic coordination and oxidation states, and therefore enable us to explore the structural evolution of crystal growth in amorphous/crystalline films associating with precursor’s structure.

Figs. 7a and b compare the surface features of the films grown at 500 and 550 °C. The surface smoothness is also of higher quality than films prepared from aluminium(III) isopropoxide [9] and acetylaceto-nate [10,23] precursors. The roughness of the latter films is probably related to the incomplete decomposition of precursors and post-deposition outgassing of organic residues, which are consistent with their high carbon contents. The average thickness of the crystalline Al2O3 film grown at 550 °C from 1 is 240 nm (Fig. 7c), and the film appears to be densely packed. It appears to consist of two layers aligned differently. The lower layer particle size is larger and more randomly arranged than the upper layer. The growth direction of the upper layer appears to be diagonal to the surface of Si substrate, as would be expected for a <1 1 3> plane.

4. Conclusion

Aluminium(III) diisopropylcarbamate has low volatility and low decomposition temperature and is a suitable metal-organic precursor for SS CVD. Clean Al2O3 film with preferred Al2O3 <1 1 3> orientation was grown at 550 °C using 1. Current work is being focused on short-range order characterization of the films, in order to improve understanding of the structural evolution in amorphous/crystalline films associating with precursor’s structure.

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References

Solvothermal approach for low temperature deposition of aluminium oxide thin films

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1. Introduction

Silicon oxide, with a band gap of 9 eV, plays a significant role as a gate dielectric in the semiconductor industry [1,2]. However, due to its low dielectric constant of 3.9 [1], the thickness of SiO2 thin film is limited in devices in which a stronger static electrical field applies. Amorphous materials have a band gap of 8.8 eV, and a dielectric constant of 9 [1]. Thin films made of Al2O3 can be used as a suitable candidate to replace SiO2 films. Furthermore, Al2O3 can endure cavitation erosion [3], so it could have a prolonged lifetime as a gate oxide.

Two chemical deposition methods using aluminium organic precursors are well studied: chemical vapour deposition (CVD) and sol-gel deposition. In CVD, films were deposited at high temperatures. Amorphous phases were typically formed at temperatures >400 °C [4,5] using commercial precursors such as aluminium triisopropoxide [4] and aluminium acetylacetonate (Alacac) [5]. Some studies have reported lower deposition temperatures of 200–400 °C [6,7] at which aluminium precursors and additional oxygen sources were required. However, a drawback was the need for a multiple control of reagent concentrations. In the sol-gel method, hydroxylated films were formed by hydrolysis of aluminium organic precursors at temperatures below 100 °C, but annealing at higher temperatures (>350 °C) [8,9] was necessary to produce Al2O3 films. These high temperature depositions are considerably expensive.

A reduction in deposition temperature requires the exploration of chemical deposition techniques. Metastable polycrystalline Al2O3 were formed at lower temperatures (<300 °C) under solvothermal conditions, whereas these polymorphs are typically obtained at temperatures >800 °C [10–13]. However, a thermodynamically controlled process to form an Al2O3 thin film has not been reported. In this work, we demonstrate the fabrication of stoichiometric and high quality Al2O3 thin films in a single step process in the liquid phase. A low deposition temperature of 65 °C could be achieved through the decomposition of a single source precursor — Al(III) diisopropylcarbamate (ADIC) by a solvothermal reaction.

2. Experimental details

A saturated solution was prepared by dissolving ADIC [14] (60 mg, 6.53 × 10⁻⁵ mol) in dry benzene (1 ml). The solution was transferred into a 23 ml Teflon liner. A Si wafer (15 × 15 mm) was immersed in the solution. The Teflon liner was capped and placed in an autoclave (Parr Instrument). The autoclave was then sealed and heated to a selected temperature for different experimental runs. The autoclave was allowed to cool after a solvothermal reaction. The Si wafer was removed from the solution and dried at 80–85 °C for the complete evaporation of benzene. A thin film appearing light blue colour was typically obtained. Films prepared at autoclave temperatures of 65, 85 and 150 °C were labelled F65, F85, F105 and F150, respectively. The internal pressures were calculated by combining the vapour pressure of benzene and air pressure at a selected temperature. They were calculated to be 1.7 atm at 65 °C, 2.4 atm at 85 °C, 3.3 atm at 105 °C and 7.5 atm at 150 °C. Film deposition was carried from 1 to
6 h. The films were characterised by X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), X-ray diffraction (XRD) and near edge X-ray absorption fine structure spectroscopy (NEXAFS).

Thermogravimetric analysis (TGA) was carried out in a Perkin Elmer Pyris 1 TGA. The sample (approx. 10 mg) was heated under N2 gas at 2 °C/min from 25 °C to 300 °C, and then at 5 °C/min up to 850 °C to ensure a complete decomposition. The flow of sheath gas was set at 20–35 ml/min at 1.38–2.41×10⁴ Pa and for balance purge at 2.76–4.14×10⁴ Pa. XPS spectra were obtained using a VG ESCALAB 220i-XL spectrometer equipped with an Al X-ray source at a background pressure of ∼1.5×10⁻⁷ Pa. A flood gun was applied to reduce a charging effect. Argon ion gun was used to etch off the surface contamination layer at a pressure of ∼2.7×10⁻⁵ Pa and at an etching speed of 2 nm/s. Curve fitting and quantification of XPS spectra were performed using CasaXPS program. Charging correction was adjusted by assuming a C₁s position at a binding energy of 285.0 eV[15,16].

The morphology of the film was observed using a Hitachi s900 SEM instrument. The film was mounted on double-sided adhesive carbon tape that was attached onto a sample holder. Silver tag and chromium coating on the surface of the film were used to enhance beam conductivity for acquiring images. SEM images were obtained at an operational voltage of 4 kV. XRD measurements of the films were carried out using Philips X’pert MRD. Cu X-ray generator was operated at 45 kV and 40 mA and supplied a Kα emission with a wavelength of 1.5418 Å. Films were scanned for 2θ axis at a step size of 0.05 ° in a continuous scan mode. NEXAFS experiments were conducted on the soft X-ray beam-line of the Australian Synchrotron under ring operation of 150–190 mA and 3 GeV. The beam-line was equipped with a collimated light plane grating monochromator SX700. The 1200 lines/mm grating and 15 μm entrance/exit slits were used. The samples were mounted on a stainless steel sample holder and characterised under a background pressure 10⁻⁷ Pa in the X-ray spectroscopy end-station. The Al X-ray absorption was measured in total electron yield (TEY) mode by monitoring drain current. A gold mesh was used to monitor photon flux incident (I₀) on the sample. The samples were characterised at a step size of 0.2 eV over the energy region 1550–1630 eV. The Al absorption peaks were calibrated in NEXAFS spectra by assuming the Al K-edge of a pure Al metal at photon energy of 1560.0 eV[16,17].

3. Results and discussion

3.1. Characterisation of Al₂O₃ thin films

The composition of the film deposited at 105 °C (F105) was investigated using XPS. Its spectrum reveals that F105 contained three elements O, C and Al at binding energies of 532.5 eV (O 1s), 285.0 eV (C 1s) and 73.9 eV (Al 2p) respectively (Fig. 1a). Nitrogen, although originally presented in the diisopropylcarbamate ligand of ADIC, was virtually absent in the film. Its absence indicates that the precursor ADIC decomposed cleanly, and the N-containing fragments were virtually removed. The concentration of C on the raw surface was found to be 13.1 atomic percentage (at.%). The bulk composition of the film was revealed by etching off a 6 nm thickness of the raw surface [15] using Ar⁺ (Fig. 1b). The C at.% was significantly reduced to 1.8 at. %, indicating the presence of C in the raw surface is not contributing to the film’s bulk composition. The O and Al contents in the film were 58.5 at.% and 39.8 at.%, respectively, giving an atomic ratio of O to Al (O/Al) to be 1.47, in agreement with stoichiometric Al₂O₃ [15,16].

High resolution SEM revealed the morphology of a typical film deposited at 105 °C for 6 h. The surface morphology shows compact Al₂O₃ particles deposited on the surface of Si wafer (Fig. 2a).
Diameters of granular particles ranging 30–60 nm are observed (Fig. 2a inset). The Al₂O₃ film appeared to be homogeneous and well adhered to the Si substrate, although some uncoated regions were also observable on the surface of the Si substrate (Fig. 2a). In Fig. 2b, SEM revealed the cross-section of film F105 to be an adhesive layer with an average thickness of 300 nm. No preferred films growth direction can be discerned. Particles are densely packed within the film.

3.2. Chemistry of the precursor’s decomposition

The solvothermal decomposition pathway at liquid phase is difficult to elucidate. Dyer et al., have found the typical decomposition products of carbamate ligands were isocyanate and alkene [18]. We propose a heterogeneous β-elimination breakdown pathway for ADIC [19] (Fig. 3 and inset). The elimination of β-hydrate led to the removal of isopropene. A pair of electrons from C–N bond breaking were localised to form a C=N bond that led to the cleavage of a C–O bond. The electron-negative O²⁻ was associated with the eliminated H⁺ to produce Al–OH fragment. Sequential dehydration at elevated pressure was thought to produce stoichiometric Al₂O₃. Decomposition of disocyanate would result in the volatile byproducts CO₂ and amine [18]. A β-elimination pathway has also been proposed during the decomposition of metal alkoxides that share similar structural characteristics [20,21]. The thermal stabilities of ADIC and Alacac (Lancaster) were investigated and compared using TGA. ADIC decomposed via a proposed β-elimination at a low decomposition temperature of 70 to 156 °C, whereas Alacac decomposed at higher temperature of 188 to 270 °C [19] through a different pathway.

3.3. Comparison of films deposited at various reaction temperatures or times

Chemical compositions of films deposited at temperatures between 65 and 105 °C were investigated. The reaction was unsuccessful at 150 °C due to a formation of dark brown precipitates which could be carbonaceous residue from pyrolysis of organic ligands. However, when the temperature was maintained at 105 °C or even lower at 65 °C, suitable films were deposited using ADIC as a single source. XPS spectra of F65, F85 and F105 showed insignificant differences in O/Al atomic ratio. The C at.% in film F105 was ~1.8 at.% comparing to ~4.4 at.% in film F65, indicating an improvement in film’s quality at higher deposition temperatures.

The effect of deposition time on films composition was examined. For film F105 deposited for approx. 1 h, the C at.% dropped substantially from 65.1 at.% in the precursor to ~4.2 at.% in the film. When the reaction was carried for 6 h, the quality of the film improved, as the C impurity was reduced to a concentration of ~1.8 at.%. This suggests that the β-elimination has been achieved within the reaction time and byproducts were effectively removed. The O/Al ratio of the films prepared over different deposition periods remained virtually unchanged at stoichiometric 1.5. The average film thicknesses varied from 150 nm to 300 nm and were independent on the reaction temperature and time.

Diffraction patterns were not observed in XRD experiments, revealing amorphous structural integrity throughout the depth of Al₂O₃ thin films. Complementary short-range NEXAFS was used to study the evolution within the films. Fig. 4 represents Al K-edge absorption spectra determined by measuring the drain current. In Fig. 4a, two absorption peaks were obtained at 1567.2 eV and 1571.5 eV. Both peaks reveal the presence of a tetrahedral (AlO₄) coordination and an octahedral (AlO₆) coordination, respectively [16]. In a native amorphous oxide structure, Al absorption peaks at 1566 eV and 1572 eV are predominant [16]. This suggests film F65 obtained at 65 °C is of purely an amorphous structure. Two peaks are found at 1569.0 eV and 1571.5 eV in film F105 (Fig. 4b) and both are absorption peaks for AlO6 coordination [16]. In comparison with NEXAFS spectrum of polycrystalline γ/β-Al₂O₃ reference [22], we noticed the appearance of a strong Al absorption peak at 1568.6 eV. This observation suggests that the AlO₆ coordination at 1569.0 eV in film F105 is an indication of a short-range crystalline structure.

4. Conclusion

In the liquid phase, Al₂O₃ films were prepared solvothermally using a single source precursor ADIC at a temperature as low as 65 °C. These stoichiometric films (carbon <5 at.%) were amorphous and of uniform and dense morphology. The proposed β-elimination that led to a successful decomposition was a necessary mechanism for the low temperature deposition. In the controls of thermodynamic parameters, the qualities of Al₂O₃ films were improved by increasing reaction temperature or reaction time. However, the thicknesses of these films were independent of the reaction temperatures and times. The future exploration on the control of the thickness of films and growth rate will be developed.

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References
