P-TYPE TRANSPARENT CONDUCTING CU-AL-O THIN FILMS PREPARED BY PE-MOCVD

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To my parents,

my husband Xinhua,

my sons Yinan and Minyi.
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Summary

This thesis reports a pioneering effort of using PE-MOCVD to fabricate highly conductive $p$-type Cu-Al-O films on quartz substrates. Special focus was put on the fabrication and the study on electrical and optical properties. The properties of the films under different growth conditions were evaluated by characterization techniques including XRD, SEM, TEM, AFM, XPS, UV-visible spectroscopy, Hall effect and Seebeck effect. Existing theories concerning conduction mechanisms were examined and new explanations were proposed. The films were proved to be truly $p$-type conductive by Seebeck measurement. The conductivity of the present thin films reached $41.0 \text{S}\cdot\text{cm}^{-1}$, the highest of $p$-type transparent conducting oxides so far achieved according to the author’s knowledge. The carrier concentration was up to $10^{19}\text{cm}^{-3}$ and the mobility was of the order of $1.0\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$. The high conductivity can be due to non-stoichiometry and codoping effects. A careful study of the temperature dependence of conductivity showed that the carrier transport generally followed grain boundary scattering of degenerate semiconductors, but for the films grown at high temperatures, it followed the thermal activation transport mechanism. Optical transmission in the UV-visible range varied greatly with the growth conditions and the direct bandgap estimated from the absorption was in the range of 3.45-4.14eV. The large bandgap could be the result of quantum confinement because the films were structured in small crystallites and amorphous states. The trend of bandgap changes can be explained by the Burstein-Moss shift and the bandgap narrowing effects. The depth profile of the film was studied by XPS. XPS spectra and peak fitting of Cu$2p_{3/2}$ revealed the existence of a great majority of Cu$^+$ and a small amount of Cu$^{2+}$ that could act as the $n$-type co-dopants.
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List of Publications


Patent

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1.1 Transparent Conducting Oxides (TCOs)

Transparent conducting oxides (TCOs) are indispensable in applications requiring contacts that are electrically conductive and optically transparent in the visible range of the light spectrum. Numerous applications dependent on transparent conducting oxides include high-resolution screens of portable computers, large flat-screen high-definition televisions (HDTVs), low emissive and electrochromic windows, thin-film photovoltaic devices (PV), and a plethora of new hand-held and smart devices, all of which need smart displays.\textsuperscript{1, 2, 3, 4, 5} The main markets for TCOs are in architectural applications and flat-panel displays (FPDs). The annual consumption of TCO-coated glass in the United States in 1996 was $7.3 \times 10^7$ m\(^2\) (or greater than 27 square miles).\textsuperscript{6} In addition to this, increasing amounts are used in displays and PVs. The volume of FPDs and hence the volume of TCO coatings continue to grow rapidly. The market for FPDs in 2000 was approximately over $15$ billion and was predicted to grow to over $27$ billion by 2005.\textsuperscript{7}

In last few years, the perception that ZnO- and InSnO- based materials were sufficient for TCO applications has begun to change. The limitations of the existing materials have been acknowledged and people have realized that new materials can open the way to new and improved devices. This is also partly stimulated by the development of high-temperature superconducting materials. Limitations of the existing materials become more critical in view of the increasing need for larger-area display devices with greater writing speeds. As the screen size of
flat-panel televisions increases, and a faster image transmission is required for portable computers, it becomes increasingly important to decrease resistivity while maintaining transparency in the TCO layers. The demand for new materials is also increased significantly due to a variety of potential new uses for TCOs such as the novel applications in more demanding environments and new heterostructure applications as parts of the all-oxide electronics. Thus TCOs are in demand not only for their electro-optical properties, but also for their interfacial and material-compatible properties. An example is the use of TCOs in a CdTe solar cell. Since the TCO film is deposited as one of the first layers of a PV cell, followed by the CdS and CdTe layers, the TCO must survive the demanding processing environment required for the rest of the cell. Recent results have shown that the use of a more stable Cd$_2$SnO$_4$ can result in significant improvements in device efficiencies. Similarly, considerable interest exists in developing $p$-type TCOs. $P$-type TCOs would open the way not only to a new generation of transparent electrical contacts for $p$-type semiconductors, but more importantly, to transparent oxide electronics when combining with $n$-type materials.

Until the start of this work, not much work was reported on the development of $p$-type TCOs, even though more applications of semiconductor devices required not only $n$-type TCOs but also $p$-type TCOs. The lack of $p$-type transparent conducting oxides has limited many applications, for example, display technology, light-emitting diodes (LED) and laser diodes (LD). In fact, from the viewpoint of the applications in semiconductor technology, a transparent $p$-$n$ junction is the key structure of a transparent functional window. The lack of $p$-type TCOs prevents the fabrication of $p$-
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$n$ junctions composed of TCOs exclusively. TCOs that are $p$-type, instead of $n$-type, would add significant new applications, if sufficient conductivity and transparency could be obtained.\(^\text{10}\)

Over the recent few years, some significant developments have come out. The group of Kawazoe \textit{et al.}\(^\text{11}\) has published papers on CuAlO\(_2\) as a truely $p$-type TCO prepared by pulsed laser deposition (PLD) since 1997. CuAlO\(_2\) thin films, although difficult to produce, are very stable. This material may offer the potential for a variety of new devices.

1.1.1 Chemical design of $p$-type TCOs

Why is CuAlO\(_2\) chosen as $p$-type TCO candidate? The answer can be found in the following. In the chemical design of $p$-type TCO materials, the first problem is how to reduce the strong localization of the positive holes at the valence-band edge of the oxide materials. This localization behavior is due to the ionicity of metallic oxides: \(2p\) levels of oxygen atoms are generally far lower-lying than the valence orbitals of metallic atoms.\(^\text{12}\) Consequently, a positive hole, if it is successfully introduced by substitutional doping, for instance, will be localized on a single oxygen anion and is unable to migrate within the crystal lattice, even under an applied electric field. In other words, the positive hole constitutes a deep acceptor level. A possible solution, chemical modulation of the valence band (CMVB), would be the introduction of covalency in the metal-oxygen bonding to form an extended valence-band structure. This is the essential characteristic of the proposed approach for obtaining $p$-type TCOs. The second problem to consider is what kind of cationic species should be selected for the introduction of covalency. The cation is expected to have a closed electronic
configuration in order to avoid coloration: transition-metal cations with an open $d$ shell are not appropriate because of strong coloration caused by $d-d$ transitions. If the energy level of the uppermost closed shell on the metallic cation is almost equivalent to that of the $2p$ level of the oxygen anion shown in Figure 1-1, chemical bonds with considerable covalency are then formed between the metal cations and the oxygen anions. Both of the atomic orbitals are occupied by electron pairs, and the resulting anti-bonding level becomes the highest occupied level, that is, a valence-band edge.

![Diagram](image)

Figure 1-1 Schematic illustration of the chemical bond between an oxygen anion and a cation (e.g. Cu$^+$) that has a closed-shell electronic configuration. (Adapted from H. Kawazoe, H. Yanagi, K. Ueda and H. Hosono, MRS Bull. 25, 28 (2000))

The two available closed-shell electronic configurations of cationic species are $d^{10}s^0$ and $d^{10}s^2$. Examples of cations with these electronic configurations are Cu$^+$, Ag$^+$, Cd$^{2+}$, In$^{3+}$, Sn$^{4+}$, and Sb$^{5+}$ for $d^{10}s^0$; and In$^+$, Sn$^{2+}$, and Sb$^{3+}$ for $d^{10}s^2$, respectively. To date, all trials to construct $p$-type TCOs from $d^{10}s^2$ cations have been unsuccessful. Hence it was inferred that the cationic species that satisfy the desired electronic structure might be Ag$^+$ and Cu$^+$. The next problem is the selection of suitable crystal structures for oxides consisting primarily of Cu$^+$ or Ag$^+$. Among the crystalline phases of Cu$^+$ or Ag$^+$, the delafossite
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structure\textsuperscript{14} was selected, whose formula is ABO\textsubscript{2}. The structure is shown in Figure 1-2.

Here A and B are a monovalent and a trivalent cation, respectively. Delafossites have a hexagonal, layered crystal structure: the layers of A cations and BO\textsubscript{2} are stacked alternately and are perpendicular to the c axis. There is no oxygen within the A cation layers and only two oxygen atoms are linearly coordinated to each A cation in axial positions. The BO\textsubscript{2} layers consist of BO\textsubscript{6} octahedra sharing edges with each other.

Each oxygen anion is in pseudo-tetrahedral coordination, as B\textsubscript{3}AO.

![Figure 1-2 Delafossite structure of ABO\textsubscript{2}, the octahedral coordination of B\textsuperscript{3+} and tetrahedral coordination of O\textsuperscript{2−} are marked. (Adapted from K. Ueda, T. Hase, H. Yanagi, H. Kawazoe, H. Hosono, H. Ohta, M. Orita and M. Hirano, J. Appl. Phys. 89, 1790 (2001))](image)

The structural characteristics of delafossites are preferable with respect to p-type and n-type TCO materials. The small coordination number of the A cations indicates that oxygen ligands are kept at a distance due to strong repulsions between 2p electrons of oxygen ligands and d\textsuperscript{10} electrons of the A cation. It is reasonable to expect from the small coordination number that the d\textsuperscript{10} electrons are lying on almost the same energy level as 2p electrons of oxygen anions. Tetrahedral coordination of the oxygen anions is also an advantage for p-type conductivity. The valence state of the oxygen anions can be expressed as sp\textsuperscript{3} in this conformation. Eight electrons (including 2s\textsuperscript{2}) of an
Chapter 1 Introduction

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oxygen anion are distributed in the four $\sigma$ bonds with the coordinating cations. The electronic configuration reduces the non-bonding nature of the oxygen anions and the localization of the valence-band edge. This expectation is strongly supported by the fact that Cu$_2$O is a $p$-type conductive oxide semiconductor, and it attracted much interest before the development of Group IV semiconductors, Ge and Si.\textsuperscript{15} It is also supported by the observation of Koffyberg et al.\textsuperscript{16} that sintered disk of Cu delafossite had $p$-type conductivity of the order of $10^{-4}$S·cm$^{-1}$.

This structure also favors the wide bandgap because the layer structure lowers the dimension of crosslinking of Cu$^+$ ions, which reduces the bandgap due to the direct interaction between $d^{10}$ electrons on neighboring Cu$^+$ ions.

In the BO$_2$ layer, B cations occupy octahedral sites and the octahedra share edges. Consequently, the distance between two neighboring B cations in the same layer is short and there are no intervening oxygen atoms on the line connecting the two cations. This structure is very advantageous for realizing $n$-type conductivity if the octahedral sites are occupied by heavy-metal cations with $s^0$ electronic configurations, such as Ga$^{3+}$ and In$^{3+}$. The appropriate combination of A and B cations in this structure may allow us to find a delafossite phase with a wide bandgap and $p$-type conductivity.

1.1.2 Plasma enhanced metal-organic CVD (PE-MOCVD)

There are mainly two complementary techniques in the deposition of TCO thin films: metal-organic vapor deposition (MOCVD) and pulsed laser deposition (PLD).\textsuperscript{17} The former process offers the attraction of in situ growth under a variety of atmospheres, the amenability to large-area coverage with high throughput and conformal coverage, the control of growth chemistry, the possibility of creating metastable structures, and
the growth of multilayers in the pulsed mode. The latter technique offers the opportunity to conveniently grow films and multilayers of almost any composition for rapid exploratory scouting. However, PLD is only suitable for small area deposition and the conductivity of the CuAlO$_2$ film reported was low. The motivation of this work is to fabricate $p$-type transparent conducting CuAlO$_2$ thin films with high conductivity and high transparency by a method suitable for mass production in industries. Plasma enhanced metal-organic chemical vapor deposition (PE-MOCVD) is a widely employed technology in wafer fabrication. This project is to explore the feasibility in using PE-MOCVD, which combines the advantages of both PECVD and MOCVD, to fabricate $p$-type copper aluminum oxide films, and to study the properties of these films.

Most chemical reactions in CVD are thermodynamically endothermic and have a kinetic energy of activation. In general this is an advantage since the reactions can be controlled by regulating the energy input. Normally the reactions in thermally activated CVD occur at a high deposition temperature.

To decrease deposition temperature, plasma is employed in the CVD process. Film deposition in a glow discharge system is a dynamically irreversible kinetic process that begins with homogeneous reactions in the plasma bulk and near the surface and terminates with heterogeneous reactions at the solid surface. The deposition processes, including the foregoing homogeneous and heterogeneous reaction sequences, are mainly controlled by the plasma properties and the excited and/or radical states. The advantages of PECVD are: low deposition temperature, high deposition rate, improved adhesion and thermal stability of deposited materials. The
low deposition temperature also favors the formation of amorphous or nano-structured deposits that often have superior properties.\textsuperscript{22} However, PECVD also has its own disadvantages. Plasmas are extremely complex chemical soups and deposition characteristics can depend markedly on system variables such as gas pressure, flow rate, RF power and frequency, reactor geometry and substrate temperature. It is, therefore, not always easy to achieve optimum control over layer properties. In addition, plasmas contain highly reactive species and the substrate is bombarded by energetic neutral and charged particles, which can cause chemical and physical damage. In the meantime, impurities are easily introduced into the film. Moreover, in the case of compounds, stoichiometry is rarely achieved. In conclusion, the advantages of plasma-enhanced CVD are considerable and it is used in an increasing number of applications.\textsuperscript{22}

As mentioned before, MOCVD has certain advantages over PLD. A key requirement for viable MOCVD processes is the availability of high-purity, thermally stable, volatile, and preferably low-melting metal-organic precursors. From the previous oxide growth studies,\textsuperscript{23, 24} known and new families of multidentate ligands that saturate the metal coordination sphere have been implemented in precursor synthesis and MOCVD growth of TCO films.

For many years, precursors for materials deposited by CVD have been restricted to simple inorganic sources. With the increasing demand for more sophisticated deposits, especially for optoelectronic materials, and the need for precise control of deposition rates, uniformity, layer properties and quality, there has been a major interest in recent years in metal-organic or organometallic precursors where the metal has been made
volatile by bonding it to organic ligands. In this project, two kinds of metal-organic precursors (acetylactonate (acac) and dipivaloylmethanate (dpm) precursors) were used.

1.2 Outline of Thesis

In this thesis, the fabrication of copper aluminum oxide films prepared by plasma-enhanced metal-organic chemical vapor deposition (PE-MOCVD) and the analysis and discussion on the properties of the films will be reported. The whole thesis has been divided into six chapters.

The first chapter presents a brief introduction of the transparent conducting oxides (TCOs) and the description of the chemical design of $p$-type TCOs. The following chapter is literature review that gives an outline and the development in the field of $p$-type transparent conducting oxides. The synthesis and the structure of CuAlO$_2$ are also introduced. Experimental details are given in Chapter 3. Systematic studies and comparisons are based on both acac and dpm precursors. Chapter 4 covers a description of the deposition of copper aluminum oxide films prepared from acac precursors and properties under different growth conditions. Many efforts are put on the analysis of structure and new explanations are proposed to illustrate the electrical and optical properties. Chapter 5 describes the properties of copper aluminum oxide films prepared from dpm precursors under different growth conditions followed by systematic analysis and discussion including conduction mechanisms, bandgap change, depth profile and valence analysis. The final chapter summarizes the main achievements of this work.
References:


Chapter 2 Literature Review

The first transparent conducting oxide was reported in 1907 by Badeker. He showed that thin films of Cd metal deposited in a glow discharge chamber could be oxidized to become transparent while remaining electrically conducting. Since then, the commercial value of these thin films has been recognized, and the list of potential TCO (transparent conducting oxide) materials has expanded to include, for example, Al-doped ZnO, GdInO₃, SnO₂, F-doped In₂O₃ and many others. Since the 1960s, tin-doped indium oxide (ITO) has been widely used for optoelectronic devices. Other TCOs are also used in large quantities for different applications. For example, tin oxide is now used in architectural glass applications. The work on the growth and characterization of semiconducting transparent oxide films has been reviewed by a few workers.

An effective TCO should have high electrical conductivity (>10⁴ S·cm⁻¹) combined with low absorption of visible light. This is achieved by selecting a wide-bandgap oxide that is made degenerate through the introduction of native or foreign dopants. Most of the useful TCOs are n-type conductors that have a wide band-gap (>3 eV), and the ability to be doped to degeneracy. When the oxide semiconductor is degenerate, an increase in carrier density leads to a widening of the bandgap due to the Burstein-Moss effect.

The state of the art in TCO performance is about 9×10³ S·cm⁻¹ with a transmittance >85 percent when averaged from 400nm to 1100nm. In general, to achieve the required transmittance, a film thickness <150nm is preferred. Typical sheet resistance...
is larger than 15Ω/sq for FPD applications and up to 100Ω/sq for touch-screen applications.

2.1 Applications of TCOs

The increasing applications of TCOs are in FPD technology and functional glass. FPDs are found in a wide variety of display applications, such as instrument panels for airplanes and automobiles, consumer electronics, video phones, displays for home appliances, televisions and video games, and displays with special requirements for the medical and military markets. The demand of the market is large. These diverse applications have varying display requirements that are met by a combination of the device design and the optical enhancement.

Transparent conducting electrodes are key components of numerous display technologies. At present, coatings of In$_2$O$_3$ doped with Sn (ITO) are employed on a massive scale for this purpose.$^{5,8}$ ITO is the most widely used TCO in FPD technology because of its easy etchability, low deposition temperature and low resistance.$^9$ However, ZnO may replace ITO in some future displays due to its lower cost and higher etchability.

The role of ITO in all FPD devices is as transparent conducting electrodes, which addresses each pixel on the display screen. While display types differ significantly, the role of ITO remains essentially the same.

In LCD structures, a sandwich structure is formed by placing a nematic liquid crystal between two glass plates. A pretreatment of the glass forces the alignment of the nematic phase at the interface in two mutually perpendicular directions and as a
consequence, the molecules rotate through the thickness of the liquid-crystal sandwich. The rotation gives rise to the acronyms TN-LCD and STN-LCD (twisted nematic and super-twisted nematic LCDs, respectively). Polarized light is guided through the structure by applying an electric field that orients the liquid crystal, and ITO is used as electrodes to apply this field.

For complex displays, the TCO is etched as stripes oriented at right angles to each other on the two substrates. The projected intersection of the two stripe planes defines the pixel position while each pixel is addressed individually.

Freezers in supermarkets pass electric current through TCOs on their display windows in order to prevent moisture in the air from condensing on the window and obscuring the view. Low cost and durability are the main factors that have led to the choice of tin oxide for this application.

An important and growing application of TCOs is electromagnetic shielding of cathode-ray tubes used for video display terminals. Shielding requirements are established by industry standards.\(^{10}\) The material requirements for this passive application are high transmissivity and modest resistivity \((2000\,\Omega/\text{sq})\), but tightening standards are driving down the resistivity requirement. The requirements for electromagnetic shielding may be addressed during the design of the anti-reflection coatings for anti-glare purposes,\(^{11}\) offering the added benefit of an anti-static function.

Functional glass for window applications ranges from passive applications of TCOs for thermal management in architectural, automotive and aircraft window glass to electrically activated structures such as electrochromic (EC) windows. In heat-efficient window applications, the TCO is used as a filter that reflects the infrared

\(P\)-type transparent conducting Cu-Al-O thin films
while remaining transparent in the visible range. For example, the TCO coatings are placed on oven windows to improve their safety as well as the energy efficiency.

In cold climates, TCO is coated on the window to reflect heat back into residential space, while in hot climates, the reverse approach is taken. So in cold climates, the plasma wavelength of TCO should be fairly long, about 2\(\mu\)m, thus most of the solar spectrum is transmitted into the building and the heat inside is reflected back. Fluorine-doped tin oxide is the best material for this purpose because it combines a suitable plasma wavelength with excellent durability and low cost as well as the high efficiency in preventing radiative heat loss due to its low emissivity. Billions of square feet of TCO-coated window glass have been installed in buildings around the world. While in hot climates, a short plasma wavelength \(\leq 1\mu\)m is desirable, so that the near-infrared portion of incident sunlight can be reflected out of the building. The metal silver and titanium nitride have sufficiently short plasma wavelengths for this application.

In high-value applications such as aircraft windows, TCO offers advantages for thermal management and may have additional functions as thin-film resistive heater elements for demisting and deicing, as antistatic coatings and as a part of antiglare thin-film stacks. Defrosting windows in airplanes was the first application of TCOs, permitting high-altitude bombing during World War II. The discovery of TCOs was kept secret until the over of the war. Tin oxide was used originally, but now ITO has replaced it in modern cockpits because its lower resistance permits defrosting larger window areas with relatively low voltage (24V).
Active functional window-glass applications include EC windows that are used for privacy, which are called smart windows. Electrically induced reduction or bleaching of certain oxides such as tungsten trioxide and vanadium pentoxide results in an electrically controllable change in color and light transmission. This effect was used in the design of smart windows that entered the market three to four years ago. The basic elements of an EC device are shown in Figure 2-1. The passage of a small current causes the initially transparent tungsten oxide to turn deep blue as a result of a change in the tungsten trioxide oxidation state. The role of TCOs in these applications is obviously as transparent conducting electrodes.

TCO-coated glass can also be used as a part of invisible security circuits for valuable works of art. TCOs like silver/ZnO multilayer also provide the best UV protection. The applications currently under development are lightweight, flexible display technologies that require the deposition of higher-performance (lower resistivity,
higher transmissivity) TCOs onto heat-sensitive polymer substrates. In several technologies, TCO is routinely deposited onto PET (polyethylene teraphthalate), polyamides and many other polymer substrates in roll-coating processes for touch-screen and IR-reflector applications. Polymer-based substrates for FPD will require the deposition of optimized TCO microstructures. The technologies in the design and implementation of flexible displays are currently under investigation.

2.2 Transparent $P$-type Conducting Oxide Films

Until now, there have been only a few reports about the preparation of $p$-type TCO films. Sato et al.\textsuperscript{12} obtained semi-transparent conducting $p$-type NiO thin films with a conductivity of 7.14S·cm\textsuperscript{-1} and a hole concentration of 1.3×10\textsuperscript{19}cm\textsuperscript{-3} by magnetron sputtering. A $p$-type ZnO\textsuperscript{13} film was reported by the simultaneous addition of NH\textsubscript{3} in carrier gas and excess Zn in the source ZnO. Its conductivity and hole concentration were typically 0.01S·cm\textsuperscript{-1} and 1.5×10\textsuperscript{16}cm\textsuperscript{-3}, respectively. However, the result was not reproducible and our group has tried various conditions with no success. Minami and his coworkers\textsuperscript{14} prepared a new multi-component oxide composed of In\textsubscript{2}O\textsubscript{3} and Ag\textsubscript{2}O by conventional RF magnetron sputtering. After post-annealing, In\textsubscript{2}O\textsubscript{3}-Ag\textsubscript{2}O thin films with Ag\textsubscript{2}O contents of 40-60wt\% exhibited poor $p$-type conduction. These films are not transparent, with the average transmittance in the visible range of about 20%. Asbalter and Subrahmanyam prepared In\textsubscript{2}O\textsubscript{3}-Ag\textsubscript{2}O thin films by reactive electron beam evaporation technique, also with poor conductivities and low transparencies.\textsuperscript{15} Significant developments of $p$-type TCOs have been reported since Kawazoe et al.\textsuperscript{16} (1997) first described a strategy for identifying oxide materials with $p$-type
conductivity and good optical transparency. The CuAlO$_2$ film was prepared by pulsed laser ablation with the $p$-type conductivity of 0.095S·cm$^{-1}$, the hole concentration of $1.3 \times 10^{17}$ cm$^{-3}$ and the transmittance of 30% to 50% in the visible region. Later, this group continued to look for new materials to verify their chemical design of TCO films. They selected SrCu$_2$O$_2$ as a candidate material, and compared non-doped and K-doped films. However, both of the films presented high resistivity and low carrier concentration even after post-annealing. After the report of Kawazoe et al. more and more attention was draw to CuBO$_2$. For example, Duan et al. prepared CuScO$_2$ by solid reaction and achieved conductivity as high as 30S·cm$^{-1}$ but with very poor transparency in the visible range. Ueda et al. later tried another compound CuGaO$_2$ by pulsed laser deposition, achieving high transparency of 80% but poor conductivity of 0.063S·cm$^{-1}$. Yanagi et al. prepared Ca-doped CuInO$_2$ by pulsed laser deposition, with very poor conductivity of 0.0028S·cm$^{-1}$.

2.3 CuAlO$_2$ Compound

2.3.1 Synthesis of CuAlO$_2$ delafossite compound

CuAlO$_2$ belongs to the group of delafossite compounds. In this group, the valences of cations A and B are +1 and +3, respectively. A could be Pt, Pd, Ag and Cu, and B could be Cr, Fe, Co, Rh, Al, Ga, Sc, In and Ti.

A variety of synthesis techniques have been found applicable for the preparation of CuAlO$_2$ with delafossite structure. In traditional ways, they generally involve either low-temperature reaction, e.g., metathesis with formation of a fused-salt by-product, or reactions under oxidizing conditions, e.g., solid-state reactions at high pressures of
internally generated oxygen. In some cases, both oxidizing conditions and low
temperatures can be advantageously used together such as in hydrothermal. A brief
description of the various methods is given below.

**Hydrothermal Reactions**

Typically hydrothermal syntheses were carried out in sealed, thin-walled platinum or
gold tubes with an externally applied high pressure and at a temperature of 500-
700°C. The length of time at the reaction temperatures was about 24 hours in all cases
and subsequently the tubes and contents were cooled at a rate of 100°/hr to room
temperature.

Powder samples of CuAlO\(_2\) could be prepared hydrothermally in basic solutions by a
method similar to that employed by Croft and his coworkers\(^2\) in their synthesis of
AgFeO\(_2\). Powder CuAlO\(_2\) was prepared at a low temperature (~500°C) by the reaction
of Cu\(_2\)O with stoichiometric quantities of Al\(_2\)O\(_3\).\(^{22}\) Shahriari *et al.* used this method to
prepare polycrystalline CuAlO\(_2\) but they could not avoid the presence of CuO and
Cu\(_2\)O.\(^{23}\) Electrical and optical properties were not given.

**Metathetical Reactions**

Reactions involving an exchange of anions between two reagent phases were found to
be particularly effective in the synthesis of Pt, Pd and Cu analogs of the delafossites at
low pressures and relatively low temperatures. These reactions usually utilized a
halide of the noble metal as one reagent and were carried out in sealed silica ampoules
at 500-700°C with no application of external pressure. By-product halide salts could
be removed after reaction by leaching with H\(_2\)O, normally leaving a single-phase bulk
delafossite product.
Solid-State Reactions
Except for Cu analogs, direct reaction of oxide reagents to form delafossite is precluded at ambient pressures because of the high temperatures necessary for solid-state diffusion, coupled with the inherent instability of the binary oxide reagents. Application of high pressure, however, permits synthesis of essentially all of the delafossite phases by this method. Susnitzky tried this method to prepare CuAlO$_2$ during reaction in air at 1100°C between CuO powder and single-crystal alumina substrates. However, no electrical and optical properties were presented.

Single Crystal Growth
This method can produce a single crystal of CuAlO$_2$ by the slow cooling of a molten mixture of Cu$_2$O and Al$_2$O$_3$ from 1200 to 1050°C. However, the size of the single crystal was not large enough to measure its conductivity and optical properties.

Sol-Gel Technique
Sol-gel technique is one kind of wet chemical synthesis methods, which is an alternative, competitive technique to obtain transparent thin films. The solution is a mixture of copper acetate hydrate, aluminum tri-sec-butoxide, ethanol and other reagents. Silica glass was dip-coated at a rate of 8cm/min, followed by drying and heating. The films had multiple phases, porous structure and quite low conductivity (up to 3.8×10$^{-3}$S·cm$^{-1}$).

Pulsed Laser Deposition (PLD)
For PLD, the CuAlO$_2$ targets were mounted on a rastered and rotating rod in a vacuum chamber and ablated with 5000 pulses from a 248nm KrF excimer laser at a repetition rate of 10Hz and a 45° of incidence angle. The substrates were attached to a resistive
heating element with silver paint and the heater was parallel to the target and placed a few centimeters away.

This method was employed by Kawazoe et al. as mentioned above, which produced CuAlO\(_2\) thin film with conductivity around 0.1S·cm\(^{-1}\) and transmission below 50% in the visible range. However, Stauber stated that it was difficult to get a pure phase by the PLD method.\(^{27}\)

**Sputtering**

Radio frequency sputtering was performed at room temperature with a single CuAlO\(_2\) target. The growth rate was approximately 100nm/h with a power of 65W and an O\(_2\) partial pressure of 34mTorr. The impurity phases CuO and CuAl\(_2\)O\(_4\) always existed and the conductivity could not be measured by the Hall instrument.

From all the above, it can be seen that the first four methods were used to prepare CuAlO\(_2\) bulk or powder samples. For these samples, the data for electrical and optical properties were either not given or very poor. The last three methods are for the preparation of thin films. For these samples, neither electrical nor optical performance was good enough to be applicable. Thus it is necessary to find another way to produce CuAlO\(_2\) thin film with better performances. As described in Chapter 1, with several advantages, the method of plasma enhanced metal-organic chemical vapor deposition was employed in this project.

**2.3.2 Structure and electrical properties of CuAlO\(_2\)**

There is a great variety of delafossites in the form of ABO\(_2\), either in the ionic radii of the B elements or in the lattice parameters.
Delafossite CuAlO$_2$ crystallizes in a layered structure that belongs to the space group $R\bar{3}m$ (rhombohedral) and a polymorphic one having the space group $P6_3/mmc$ (hexagonal). The trivalent ions Al$^{3+}$ are located at the center of regular oxygen octahedra that are inclined and connected by monovalent ions Cu$^{+1}$. Normally, $R\bar{3}m$ was described referring to a hexagonal axis. Such a hexagonal description favors the view of delafossite structure as layers instead of oxygen octahedra$^{28}$ (Figure 2-2).

![Figure 2-2](image)

Figure 2-2 The delafossite structure where the Cu$^+$ cation (small dark sphere) is in two-fold linear coordination to oxygen (large sphere) and the Al$^{3+}$ cation (small light sphere) is in octahedral coordination. The c-axis is vertical. (Adapted from R. Nagarajan, N. Duan, M. K. Jayaraj, J. Li, K. A. Vanaja, A. Yokochi, A. Draeseke, J. Tate and A.W. Sleight, Int. J. Inorg. Mat. 3, 265 (2001))

The hexagonal description can be viewed as a sequence of planes with different ions in the order of O$^{2-}$- Al$^{3+}$- O$^{2-}$- Cu$^{+}$- O$^{2-}$- Al$^{3+}$- O$^{2-}$. The key structure of delafossite CuAlO$_2$ is that both Cu and Al atoms form triangular arrays. The $R\bar{3}m$ rhombohedral delafossite contains three CuAlO$_2$ molecules per unit cell and has lattice constants $a$
and $c$ around 2.87Å and 17Å, respectively.\textsuperscript{29} For $P6_3/mmc$, the lattice constants $a$ and $c$ are around 2.86Å and 11.3Å and only two CuAlO$_2$ are found in the unit cell.\textsuperscript{30}

Rogers and his coworkers\textsuperscript{31} noted that when A was Pd or Pt, the oxides were conducting (the in-plane conductivity of PtCoO$_2$ was in the order of $10^6$S·cm$^{-1}$, only slightly smaller than Cu metal) but Cu- and Ag- based delafossites were semiconducting. And the conductivity was expected to be highly anisotropic because of the layer structure. However, this phenomenon was not observed in polycrystalline CuAlO$_2$ as expected\textsuperscript{32} so Benko and Koffyberg interpreted their data by neglecting the structural anisotropy and regarded that the deduced parameters would represent average values. As described in last section, the conductivity of the CuAlO$_2$ samples was normally not very good and it was up to 0.1S·cm$^{-1}$. 
References:

Chapter 2 Literature Review


Chapter 3 Experimental Details

3.1 Thin Film Deposition Equipment

The exact arrangement of a CVD apparatus can vary widely depending on the particular applications. The basic main components of a PE-MOCVD apparatus can be thought of as being made up of two main constituent parts: the transportation system and the reactor.

3.1.1 Transportation system

The reagent-handling system mixes and meters the gas mixture to be used in the reactor unit. The design depends on the source compounds. Gaseous sources such as SiH$_4$ are fed from a high-pressure gas cylinder, through a mass flow meter. A carrier gas in a bubbler is typically used for liquid and solid sources. The carrier gas flow rate and the pressure over the source will determine the amount of reagents being transported from the bubbler. If thermodynamic equilibrium is established in the bubbler, the flow rate of the reagent (F) is given by

$$F = F_{\text{carrier}} P / (P_{\text{total}} - P)$$

where $P$ is the partial pressure of the source.

In the present system (see Figure 3-1), the metal-organic precursors are in the solid state. The precursors in a half opened quartz tube are transported continuously (Figure 3-2) to the heating region, sublimated by being heated with a halogen lamp and then carried by argon gas to the reactor. The heating region is a quartz tube with halogen lamp above. The light from the lamp focuses on the precursors through the quartz tube.
wall, which causes the sublimation of the precursors. The temperature of the external wall of the quartz tube is kept at around 150°C. The gas line for precursors transportation is also heated to 150°C to prevent the solidification of metal-organic precursors. The reactive gas (oxygen) is fed from a high-pressure gas cylinder through a mass flow meter and then mixed with precursors before the gases enter the reactor. In Figure 3-2, it can be seen that the half opened quartz tube is fixed in an iron holder, which can be attracted by a magnet and the magnet is driven by a stepping motor.

Figure 3-1 Schematic diagram of transportation system.

Figure 3-2 Schematic diagram of precursors transportation tube.
3.1.2 Reactor

The reactor is the heart of any CVD system and as termed, a malfunction or failure of this vital organ can have disastrous consequences.

There are a variety of reactors. The horizontal and vertical reactors are classical configurations for atmospheric and reduced pressure growths. They are primarily used in research and for the growth of compound semiconductors by organometallic vapor phase epitaxy (OMVPE). The barrel reactor is the primary means of silicon epitaxy and small barrels are employed in GaAs technology. The pancake reactor is being used extensively in silicon technology and a pancake-type reactor with multi-wafer planetary motion has recently been introduced for OMVPE. The reactor walls are typically cooled to minimize particulate and impurity problems caused by the deposition on the walls. Low pressure CVD is the main production tool for polycrystalline silicon, dielectric and passivation films used in silicon-based microelectronics manufacture.

In this project, plasma enhanced CVD (PECVD) is employed. A PECVD reactor has several basic components: a vacuum chamber and a pumping system to maintain reduced pressure, a power supply to create the discharge, a temperature control system, and gas or vapor handling facilities to meter and control the flows of reactants and products. In general, four basic reactor configurations are normally used to deposit films by PECVD: capacitively coupled, inductively coupled with substrates downstream of the discharge, inductively coupled with substrates within the glow region, electron cyclotron resonance configuration. The most common systems are the capacitively coupled arrangements where the substrates can be mounted horizontally
or vertically in a diffusion tube. The vertical design is often favored because a larger number of substrates can be accommodated in a relatively small reactor volume. In both configurations the substrates are immersed in the glow discharge, and subjected to electron, photon, and ion bombardment. In the present system, the capacitively coupled design is used. Below is the schematic diagram (Figure 3-3) of the reactor.

![Diagram](image)

Figure 3-3 Schematic diagram of the reactor of the PECVD system employed in this project.

The whole reactor is cylinder shape and made of stainless steel. There are three heaters mounted symmetrically inside. Substrates can be placed on any heater. Argon gas carries sublimated precursors to the central tube where it mixes with reactive gas oxygen, and then they enter the chamber together. The tube outside the chamber is
heated to prevent consolidation of precursors. The gases diffuse to the substrates and the by-products and exhaust are pumped to the fume hood. The first level vacuum system is a rotary pump and the second level is a turbo-molecular pump, which can keep the chamber at a high vacuum of $3 \times 10^{-6}$ Torr.

There are two types of plasma currently used in CVD: glow-discharge plasma (non-isothermal) and arc plasma (isothermal).\(^3\) A glow-discharge plasma (non-isothermal) is generated in a gas by a high-frequency electric field, such as microwave (2.45GHz), at a relatively low pressure. In such a plasma, the following events occur: in a high-frequency electric field, the gases are ionized to form electrons and ions; the electrons, with their extremely small mass, are quickly accelerated to high velocity with energy levels corresponding to a temperature of 5000K or higher;\(^4\) the heavier ions with their much greater inertia cannot respond to the rapid changes in field direction so their temperature, and that of the plasma, remain low, as opposed to the electron temperature (hence the name non-isothermal plasma); the high-energy electrons collide with the gas molecules resulting in dissociation and generation of reactive chemical species and the initiation of the chemical reactions. The most common frequencies used for CVD are the microwave at 2.45GHz and radio frequency (RF) at 13.56MHz.\(^3\) The typical equipment of RF plasma consists of parallel electrodes as shown in Figure 3-3, and this is used for the work in this project.

The temperature range of the reactor is from room temperature to 850°C. There is a thermocouple just under the susceptor and a temperature controller regulates the temperature. All the temperature controllers used in our system are SR70 series made by Shimaden Co. Ltd of Japan.
The handling of precursors was explained in the previous section. The carrier gas Ar and the reactive gas O₂, both with the purity of 99.99%, are from a commercial compressed gas tank and the gases are measured by separate flow meters. The model of the flow meters is D08-4B/ZM from Beijing Jianzhong Machine Factory of China.

3.2 Characterization of Thin Films

3.2.1 Electrical testing equipment

There are two ways to measure resistance: four-probe method and two-probe method. We used the four-probe method to measure the resistivity/sheet resistance at room temperature and the two-probe method to measure the change of resistance with temperature.

In the four-probe method, a four-point metal-tip probe assembly is pressed on the surface as shown in Figure 3-4. The outer probes are connected to the current source, and the inner probes detect the voltage drop.

![Figure 3-4 The four-probe method for sheet resistance measurement of a film.]

For equal probe spacing, the sheet resistance \( R_s \) is given simply by

\[
R_s = \frac{\pi V}{\ln 2 I} = 4.53 \frac{V}{I} = 4.53 R
\]  

\[\text{(3-2)}\]
This equation is valid as long as the film thickness is much thinner than the probe spacing and the sample size is much larger than the probe spacing. This is a standard method widely used.

Below is a self-designed system for the measurement of the change of resistance with temperature (shown in Figure 3-5). A two-stage pumping system with a mechanical rotary pump and a diffusion pump was used to obtain the high vacuum of $10^{-6}$Torr to prevent oxidation of the films. Thermal heating and electrical testing were available in this high vacuum system. A k-type thermocouple with a temperature control unit was used to monitor and control the temperature change. The resistance change with temperature is monitored via an in-situ two-point probe system.

Figure 3-5 Schematic of simplified high vacuum system for measuring temperature dependence of resistance.
3.2.2 X-ray diffraction (XRD)

X-ray diffraction (XRD) is a versatile, non-destructive analytical technique for identification and quantitative determination of the various crystalline forms, known as ‘phase’, of compounds present in solid samples. The identification is achieved by comparing the X-ray diffraction pattern (or ‘diffractogram’) obtained from an unknown sample with an internationally recognized database containing reference patterns for more than 7000 phases.

An incident monochromatic X-ray impinging on a crystalline structure is diffracted if the X-ray beams scattered by adjacent crystal planes are in phase (constructive interference) according to the Bragg’s equation

\[ 2d \sin \theta = n \lambda \]  

where \( \lambda \) is the wavelength of X-rays, \( \theta \) is the angle of scattering (Bragg angle), \( d \) is the spacing between adjacent crystal planes, and \( n \) is an integer that represents the order of diffraction.

For crystalline materials, characteristic diffraction peaks are obtained. Each peak represents diffraction of the X-ray beam by a set of parallel crystal planes \((hkl)\). For amorphous materials, a broad diffused pattern is obtained due to the inherent short-range order.

For the current work, a PHILIPS X’Pert-MPD PW3040 was used to characterize all the thin film samples. The X-ray source used was Cu-K\(_\alpha\) of wavelength 1.5418Å. This PW3040 system is equipped with a thin film attachment, which can be used for phase analysis of polycrystalline thin film layers (minimum thickness 100Å on a substrate). In thin film analysis it is important to enhance the signal intensity of the film as much
as possible. This can be achieved by setting the incidence angle to a small value, resulting in a considerable amount of the radiation from the X-ray tube being diffracted by the film. This means that the optics of the thin film diffractometer is not symmetrical in this application. The main differences compared with a symmetrical (0-2θ scan) diffractometer are:

a) the use of a fixed angle of incidence, for example, 0.5° to 3°, combined with a narrow divergence slit of such as 1/32, 1/16, or 1/8 degree;

b) the employment of a collimator instead of a receiving slit, because the diffracted beam is almost parallel and not focused, unlike that in a normal diffractometer;

c) a 2θ scan instead of a 0-2θ scan, to determine the position and intensity of the diffraction peaks.

![Diagram of the thin film diffractometer](image)

Figure 3-6 The principles of the thin film diffractometer.
Figure 3-6 is an illustration of the principles of thin film analysis. In this study, a fixed 1° incidence angle ($\theta_1$) with a narrow divergence slit of 1/8 degree was used for the sample analysis. The samples were normally scanned with a diffraction angle $2\theta$ from 10° to 80° at a scanning step size of 0.03°.

### 3.2.3 UV-visible spectroscopy

Spectrophotometry involves the measurement of light transmission and absorption of a sample. UV-visible spectrophotometry, as the name implies, thus involves the measurement with wavelengths in the region of about 200–1100nm. This encompasses the near ultraviolet (UV) region (200–400nm), the visible range (400–700nm) as well as the near infrared (IR) region with wavelengths between 700 and 1100nm. A common characteristic of such radiations is that they induce transitions in the outermost shell of the molecules under study, and generally do not damage the sample. Hence UV-visible spectrophotometry may be regarded as a non-destructive technique. The samples obtained were subjected to transmittance and absorption measurements using a Shimadzu UV-1601 UV-visible spectrophotometer. The fast scanning mode (with a sampling interval of 1.0nm) and a slit width of 2.0nm were used for the measurement.

To measure the absorption spectrum of a compound X, it must be ensured that any variation in the signal observed is due to the absorption of light by X itself. The true absorption spectrum of the compound X in question is thus obtained by:

(i) measuring the spectrum of all components in the system in the absence of X (i.e., determining the baseline),

(ii) measuring the spectrum of all components in the system with X present, and
(iii) subtracting the baseline from the spectrum obtained in step (ii).

Figure 3-7 shows a schematic of a double beam spectrophotometer similar to the aforementioned Shimadzu UV-1601 model.

Figure 3-7 Schematic of a double beam spectrophotometer. (Adapted from D. A. Harris, Light Spectroscopy, Bios Scientific Publishers Ltd., Guildford (1996))

In the double beam instrument, a spectrum can be adjusted for baseline absorption in a single measurement, where the sample is placed in the path of the ‘measuring beam’, and a blank reference in the path of the reference beam. The resulting signal directly records the difference between the sample and the baseline, thus obtaining the spectrum of the component X itself.

The principle of operation is that an illuminating beam from a tungsten-halogen lamp or a deuterium lamp (depending on the wavelength) is split into two beams that fall on the sample and the reference. A single monochromator then selects the wavelength of the beam, and a chopper switches the beam from the sample to the reference at the rotational frequency of the chopper. The light is focused on the same area of the single detector (photo-multiplier) in order to ensure that each beam is monitored with the same sensitivity. A signal from the chopper instructs the electronics, thus enabling the sample and reference beams to be compared.
3.2.4 Hall effect

The Hall effect is based upon the deflection of moving charge carriers. Consider a sample in the form of a rectangular bar as shown in Figure 3-8 (i) below. An electric field $E$ is applied in the x-direction while a magnetic field $B$ is applied along the z-direction. According to Lorentz’s law, the force acting on the charged particle will then be given by $F = q (v \times B)$, where $v$ is the velocity of the particle and $q$ is its charge. The Lorentz force $F$ is thus a vector perpendicular to both $v$ and $B$ in a right-handed direction (i.e., in the y-direction for this case). Hence, free charge carriers will be deflected to the same side, resulting in a separation of charge across the two opposite sample surfaces perpendicular to the y-axis. An electric field, $E_{HH}$, called the Hall field, is thus created across these sample surfaces.

![Figure 3-8 Sample geometries for performing Hall measurements. (i) Bar-shaped specimen, (ii) thin film sample and (iii) clover-shaped sample used in the Van der Pauw method. (Adapted from P.Y.Yu and M.Cardona, Fundamentals of Semiconductors, Springer-Verlag, Berlin (1996))](image)

The Hall field may be expressed in terms of the current density $J$ as

$$E_{HH} = R_{HH}JB$$

---

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where $R_H$ is defined as the Hall coefficient, which is related to the density of charge carriers $n$ by

$$R_H = \frac{1}{ne} \quad \text{(3-5)}$$

The sign of $R_H$ depends on the sign of the charge, and is negative for electrons and positive for holes.

One limitation of the Hall effect measurement described above is that the sample must be in the form of a rectangular bar as in Figure 3-8 (i). Van der Pauw developed the Hall technique to the measurement of thin film samples. Two common geometries for the Van der Pauw method of Hall effect measurement for a thin sample are shown in Figure 3-8(ii) and (iii). The method shown in Figure 3-8(ii) is particularly convenient for a disk of irregular shape. Current is fed through contacts 3 and 4 while the voltage is measured across contacts 1 and 2. The “clover” shape in Figure 3-8 (iii) has the advantage of keeping the current flow away from the voltage contacts. To minimize the error in the measurement of the Hall voltage (as current flow may not be perpendicular to the line joining contacts 1 and 2), both the voltage with the magnetic field $V_{12}(\pm B)$ and without the magnetic field $V_{12}(0)$ are usually measured. Van der Pauw showed that the Hall coefficient is given by

$$R_H = \frac{\left[ V_{12}(B) - V_{12}(0) \right] d}{I_{34}B} = \frac{\left[ V_{12}(B) - V_{12}(-B) \right] d}{2I_{34}B} \quad \text{(3-6)}$$

where $d$ is the thickness of the film, $B$ is the magnetic field and $I_{34}$ is the current flowing from contact 3 to contact 4.

The sample resistivity $\rho$ can also be measured with the Van der Pauw method. In this case two adjacent contacts such as 2 and 3 ($I_{23}$) are used as current contacts while the
two remaining contacts are used for measuring the voltage drop \( V_{41} \). The resulting resistance is defined as \( R_{41, 23} \):

\[
R_{41, 23} = \frac{|V_{41}|}{I_{23}} \tag{3-7}
\]

Another measurement is further made, in which the current is sent through contacts 1 and 3 \( (I_{13}) \) instead while the voltage is measured across contacts 2 and 4 \( (V_{24}) \). From the resulting resistance \( R_{24, 13} \), together with the previously obtained \( R_{41, 23} \), \( \rho \) can be calculated with the expression,

\[
\rho = \frac{\pi d (R_{24, 13} + R_{41, 23}) f}{2 \ln 2} \tag{3-8}
\]

where \( f \) is a factor that depends on the ratio \( R_{24, 13}/R_{41, 23} \) and \( f \) is equal to 1 when the ratio is exactly 1 and decreases to 0.7 when the ratio is 10. Usually a large value for this ratio is undesirable, and \( R_{24, 13}/R_{41, 23} \) is kept nearly 1 in this work.

The description of the Hall effect for the presence of two types of free carriers can be found in Appendix C.

### 3.2.5 Scanning electron microscopy (SEM) and energy dispersive X-ray analyzer (EDX)

Surface morphologies and cross–section images of the samples were studied by a PHILIPS XL30-FEG (Field Emission Gun) scanning electron microscope (SEM), equipped with an Ion Getter Pump (IGP), which enables the normal working pressure for the source to achieve about \( 2 \times 10^{-9} \)Torr or better. An energy dispersive X-ray analyzer (EDX) attached to the SEM enables the detection and identification of the X-ray produced by the impact of the electron beam on the film, thereby allowing qualitative and quantitative elemental analysis.
The SEM has a large depth of field and it produces high magnification images.\textsuperscript{10} The combination of high magnification, large depth of field, great resolution, and ease of sample observation makes SEM one of the most heavily used instruments in research and industry areas.

The most widely used signal in the SEM is from secondary electrons. Secondary electrons are produced by the interactions between incident electrons and weakly bound conduction band electrons in the atoms of the sample. The average energy of secondary electrons is quite low so they are easily collected by being attracted by a positive charge.

An energy-dispersive X-ray analyzer (EDX) is a common accessory that gives the SEM a very valuable capability for elemental analysis.\textsuperscript{11} The electron beam in a SEM has an energy typically between 5keV and 20keV. The binding energy of the electrons in atoms ranges from a few eVs up to many keVs. Many of these atomic electrons are dislodged as the incident electrons pass through the specimen, thus ionizing atoms of the specimen. An atomic electron is ejected by an electron in the beam and the ionized atom is then quickly neutralized by other electrons. In the neutralization process, an X-ray with an energy characteristic of the parent atom is emitted. By collecting and analyzing the energy of these X-rays, the constituent elements of the specimen can be determined.

For the EDX study, the working distance was kept at 10mm. Voltage and spot size were adjusted to make the Counts per Second (CPS) in the range of 1000 to 2000.
3.2.6 X-ray photoelectron spectroscopy (XPS)

X-ray Photoelectron Spectroscopy (XPS) was developed in the mid-1960s by Kai Siegbahn and his co-workers at University of Uppsala, Sweden. This technique was first named by the acronym ESCA (Electron Spectroscopy for Chemical Analysis). Surface analysis by XPS\textsuperscript{12} involves irradiating a solid in vacuum with monoenergetic soft X-rays and analyzing the emitted electrons by energy. The spectrum is obtained as a plot of the number of detected electrons per energy interval versus their kinetic/binding energy. Each element has a unique spectrum. The spectrum from a mixture of elements is approximately the sum of the peaks of the individual constituents. Because the mean free path of electrons in a solid is very small, the detected electrons originate only from the top few atomic layers, making XPS a unique surface-sensitive technique for chemical analysis. Quantitative data can be obtained from peak heights or peak areas, and identification of chemical states can often be made from the measurement of exact positions and separations of peaks, as well as from certain spectral features.

In this thesis, Mg K\(\alpha\) (1253.6eV) X-ray was used and the equipment model is a VG ESCLALAB MKII. The photons interact with atoms, causing electrons in the surface region to be emitted by the photoelectric effect. The emitted electrons have kinetic energies of \(KE = \nu - BE - \phi_s\), where \(\nu\) is the energy of the photon, \(BE\) is the binding energy of the atomic orbital from which the electron originates and \(\phi_s\) is the work function that is normally taken into consideration by the machine prior to the data collection. The binding energy may be regarded as the energy difference between the initial and final energy states as the photoelectron leaves the atom. Because there are a
variety of possible final states of the electrons from each type of atom, there are a corresponding variety of kinetic energies of the emitted electrons. Moreover, there is a different probability or cross-section for each final state. Because each element has a unique set of binding energies, XPS can be used to identify and determine the concentration of the elements in the surface. Variations in the elemental binding energies (the chemical shifts) arise from the differences in the chemical potential and polarizability of the compounds. These chemical shifts can be used to identify the chemical state of the material being analyzed.

Figure 3-9 The XPS emission process (left) for a model atom. An incoming photon causes the ejection of the photoelectron. The relaxation process (right) for a model atom results in the emission of a KL23L23 electron. The simultaneous two-electron coulombic rearrangement results in a final state with two electron vacancies.

In addition to photoelectrons emitted in the photoelectric process, Auger electrons can be emitted because of the relaxation of the excited ions remaining after the photoemission. An Auger electron emission occurs roughly $10^{-14}$ seconds after photoelectric event. In the Auger process, an outer electron falls into the inner orbital vacancy, and a second electron is simultaneously emitted, carrying off the excess energy. The Auger electron possesses kinetic energy equal to the difference between the energy of the initial ion and the doubly charged final ion, and is independent of the
mode of the initial ionization. Thus, photo-ionization normally leads to two emitted electrons (a photoelectron and an Auger electron (Figure 3-11)). The sum of the kinetic energies of the electrons emitted cannot exceed the energy of the ionizing photons.

3.2.7 Transmission electron microscopy (TEM)

The transmission electron microscope (TEM) was first developed in the 1930's after it was apparent that the wavelength has an effective role on the theoretical resolution. Green light, which is used for the optical microscope has a wavelength of 0.5\( \mu \)m and therefore has a theoretical resolution of about 0.2\( \mu \)m. As the electromagnetic spectrum moves to shorter wavelengths, an ultraviolet microscope with a theoretical resolution 0.05\( \mu \)m could be used. X-ray microscopes would have a vastly superior increase in resolution, but X-rays cannot be easily refracted to form an image. Electron waves offer the best alternative. The electron could be easily refracted in a magnetic field and accelerated by an electrical potential. The stronger the potential the faster the electron will move and, from the de Broglie relationship, the shorter the wavelength therefore the better the resolution. In fact a typical electron microscope at an accelerating voltage of 75kV would have a wavelength less than 5 picometers. This makes the theoretical resolution about hundred thousand times better than that of light. Unfortunately, the TEM resolution has never reached this theoretical resolution. This is because the magnetic fields cannot be manipulated, shaped and grouped the same way as the glass lenses. Therefore, aberrations are difficult to remove, leading to the poorer resolution in comparison with the theoretical one.
Chapter 3 Experimental details

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The TEM can provide two separate kinds of information about a specimen: electron diffraction patterns and high resolution images. To obtain an electron diffraction pattern, a beam of electrons impinges on a crystalline specimen. Some of the electrons pass through the specimen without interaction and hit the screen or film which is a distance L from the specimen. Other electrons are diffracted through an angle \( \theta \) by the crystal planes of spacing d and then hit the screen or film. From simple geometry, it is obtained that\(^\text{13} \)

\[
rd = L\lambda
\]

where \( \lambda \) is the electron wavelength, \( r \) is the distance of a diffraction spot from the undiffracted spot. As \( L \) and \( \lambda \) are both independent of the specimen, \( L\lambda \) is called camera constant. After knowing \( L\lambda \) and \( r \), spacing \( d \) can be calculated. Different microstructures will show different diffraction patterns. To obtain a high resolution image, a large aperture allowing several beams to pass through is employed. In the present study, an atomic-resolution TEM (Philips CM300 FEG-TEM) with a resolution limit of 1.7Å was used.
References:


Chapter 4 Properties of Cu-Al-O Films Grown from Acetylacetonate Precursors

4.1 The Selection of Precursors

Metal-containing precursors are often used for growing metal-containing films by CVD. Such precursors should have a reasonable vapor pressure at a temperature that does not lead to thermal decomposition, and they should undergo thermal decomposition in a controlled manner (by eliminating organic byproducts). As a rule of thumb, a vapor pressure of at least 100 mTorr is desirable at the delivery temperature to achieve reasonable deposition rates. Metal-containing compounds can be classified into three categories, depending on the nature of the ligands attached to the metal center: (1) inorganic compounds, which possess ligands that do not contain carbon; (2) metal-organic compounds, which possess ligands that contain carbon but do not possess metal-carbon bonds; and (3) organometallic compounds, which possess carbon-containing ligands with metal-carbon bonds. Inorganic compounds that have been used as precursors are primarily metal halides. They typically have low volatility (with a few exceptions, such as TiCl₄ and WF₆), and high temperatures are required to initiate reactions. In addition, a co-reagent (such as H₂) is generally required to produce the final desired film. Metal-organic and organometallic compounds are much more preferred than inorganic compounds due to their higher volatility.

β-diketonate ligands are bidentate and generally prefer to chelate to a metal center, and metal β-diketonate complexes of low-coordination-number metals are often monomeric and volatile.¹ Therefore, metal β-diketonates, owing to their relatively
high volatility, are widely applied as precursors in CVD for the production of oxide and metal films. The general formula of metal β-diketonate is M(RC(O)CHC(O)R')\(_x\), where M is the metal, x is its valence, R and R' are end substituents. When R=R'=CH\(_3\), the compounds are called metal acetylacetonates (acac), which are the precursors for the films grown by CVD described in this chapter. When R=R'=C(CH\(_3\))\(_3\), the compounds are called metal dipivaloylmethanates (dpm), which will be the precursors used in the work described in the next chapter.

![Figure 4-1 Structures of (a) copper and (b) aluminum acetylacetonate precursors.](image)

The 2-dimensional structures of Cu(acac)\(_2\) and Al(acac)\(_3\) are shown in Figure 4-1. The thermolysis products of Cu(acac)\(_2\) at high temperature are molecular ions of reaction products such as acetylacetone, acetone, ketene, methylethylketone, carbon oxides, water, methane and CH\(_3\)C(O)CH=CO. This process proceeds in three parallel directions depending on temperature:\(^2\)

\[T<T_d: \text{solid phase} + \text{CH}_3\text{C(O)CH}_2\text{C(O)CH}_3, \text{CH}_3\text{C(O)CH}_3, \text{CH}_3\text{C(O)C}_2\text{H}_5, \text{CH}_2\text{CO, CO} \]

\[T>T_d: \text{solid phase} + \text{CO, H}_2\text{O} \]

\[T>400^\circ\text{C}: \text{solid phase} + \text{CH}_3\text{C(O)CH}=\text{CO}, \text{CH}_4 \]
where \( T_d = 230 \pm 10^\circ C \) is the temperature of the thermolysis onset (so-called threshold temperature) of Cu(acac)_2. The thermolyses in the presence of hydrogen and oxygen proceed similarly. However, in the latter case the thermal oxidative decomposition of reaction products (in particular, acetylacetone) is imposed on the thermolysis of the complex at a temperature above 300\(^\circ\)C. It results in an increase in the relative content of carbon oxides and water in comparison with the vacuum case. The thermolysis threshold temperature significantly increases (about 50\(^\circ\)C) in the presence of hydrogen, but no hydrogen influence on the composition of gaseous products and the thermolysis mechanism is observed. Al(acac)_3 has been widely used in the deposition of Al_2O_3.\(^3,4\) The perceived advantages of Al(acac)_3 over other aluminum precursors include lowered-toxicity, good stability at room temperature, easy handling, high volatility at elevated temperatures and low cost. Similar to Cu(acac)_2, the main thermolysis products of Al(acac)_3 are acetone and carbon dioxide.

In this chapter, the characterization results of the films prepared from acetylacetonate precursors will be presented and the properties of the films will be discussed.

### 4.2 Experimental

Cu-Al-O films were prepared in a 13.56MHz RF plasma enhanced CVD apparatus. Mixed metal-organic precursors Cu(acac)_2 and Al(acac)_3 of a mole ratio 1:1 were sublimated at about 150\(^\circ\)C. The vapor was then carried by Ar gas into the reaction chamber. The reactive gas, O_2, was introduced into the chamber through another inlet. Mass flow controllers were employed to maintain the flow of both the carrier and reactive gases. By using a turbo molecular pump, a base pressure of \( 3 \times 10^{-6} \)Torr of the
reactor was obtained. The substrates employed (quartz plates of dimension 10mm×10mm) were cleaned by successive ultrasonic cleaning in analytically pure ethanol, acetone and ethanol before they were introduced into the reactor. Prior to the deposition, the substrates were heated at 400°C for 1 hour for further thermal cleaning and degassing. The deposition parameters employed were: substrate temperature at 630-800°C, flow rate of reactive gas O₂ at 4-25sccm, flow rate of carrier gas Ar at 18-30sccm, RF discharge power at 50-200W, and pressure at 7.5×10⁻² or 1.5×10⁻³Torr.

The morphology of the film was examined using a field-emission scanning electron microscope (SEM) (Philips XL30 FEG-SEM). The thickness was measured by an Alpha-step 500 surface profiler or/and by cross-section SEM. An X-ray powder diffraction (XRD) apparatus (Philips X’pert-MPD) and an atomic-resolution transmission electron microscope (TEM) (Philips CM300 FEG-TEM) were employed to reveal the structure of the sample. The type of conductivity was determined by employing the Hall-effect method (BIO-RAD HL5500PC) and the Seebeck technique. The chemical composition in the film and the valence of copper were observed by X-ray photoelectron spectroscopy (XPS) (VG ESCALAB MKII) and the stoichiometry was estimated by energy dispersive X-ray spectroscopy (EDX) (Philips XL30 FEG-SEM). The transmittance and absorbance of the film were measured by employing the Shimadzu UV-1601 UV-visible spectrophotometer.

The following parts will first discuss the properties of a typical film with $p$-type conductivity and then describe the effects of parameters including substrate temperature and oxygen flow rate on the properties of the films. A further discussion is given in the last section.
4.3 Results and Discussion

4.3.1 A typical sample

In this part, the results of the most conductive sample prepared from acetylacetonate precursors will be presented. In the growth process, the substrate temperature was 745°C, the O₂ flow rate was 25sccm, the Ar flow rate was 18sccm, the RF discharge power was 200W, and the working pressure was 75mTorr.

The film thickness was estimated to be 250nm by cross-section scanning electron microscopy. Efforts were made in using XRD for the identification of phases in the sample. Figure 4-2 shows characteristic peaks of the film. The peaks are magnified by using a logarithmic y-axis. The inset of Figure 4-2 is plotted in linear y-axis, in which the humps and small peak are hard to identify.

![XRD Spectrum](image)

Figure 4-2 XRD spectrum of the film prepared at 745°C from acac precursors, the intensity is plotted on a logarithm scale. The inset is a plot using linear y-axis.

There were three obvious peaks at 43.34° (2.086Å), 50.53° (1.807Å) and 74.21° (1.278Å), a big hump around 21.20° (4.208Å) and two small humps around 36.50°
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(2.463Å) and 64.40° (1.447Å) (the value in the bracket is the lattice spacing d corresponding to the 2θ value). The hump around 21.20° (4.208Å) was attributed to the quartz substrate, but not excluding the possibility of β-CuAlO₂ that contains a peak at 21.50°.

Table 4-1 Lattice spacings (Å) determined from XRD (Experimental data), and the corresponding lattice spacings (LS) of relevant materials (CuAlO₂, Al₂O₃ and Cu) from PDF. (LS data in bold are very close to the experimental data).

<table>
<thead>
<tr>
<th>Peak</th>
<th>Experimental data (Å)</th>
<th>LS/ plane CuAlO₂</th>
<th>LS/ plane CuAlO₂</th>
<th>LS/ plane Al₂O₃</th>
<th>LS/ plane Cu</th>
<th>LS/ plane Cu</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>4.208</td>
<td>4.120</td>
<td>--</td>
<td>--</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>2</td>
<td>2.463(hump)</td>
<td>2.470</td>
<td>2.479/(100)</td>
<td>2.466/(101)</td>
<td>2.381/(110)</td>
<td>--</td>
</tr>
<tr>
<td>3</td>
<td>2.088</td>
<td>2.100</td>
<td>2.072/(103)</td>
<td>2.010/(015)</td>
<td>2.087/(113)</td>
<td>2.080/(111)</td>
</tr>
<tr>
<td>4</td>
<td>1.807</td>
<td>1.820</td>
<td>1.864/(104)</td>
<td>1.739/(107)</td>
<td>1.741/(024)</td>
<td>1.810/(200)</td>
</tr>
<tr>
<td>5</td>
<td>1.447(hump)</td>
<td>1.447</td>
<td>1.432/(110)</td>
<td>1.439/(110)</td>
<td>1.405/(214)</td>
<td>--</td>
</tr>
<tr>
<td>6</td>
<td>1.278</td>
<td>1.271</td>
<td>1.277/(114)</td>
<td>1.283/(116)</td>
<td>1.277/(208)</td>
<td>1.281/(220)</td>
</tr>
</tbody>
</table>

I PDF file 21-0276, which lacks information of structure, space group and indices
II PDF file 77-2494, structure-Hexagonal, space group- P6₃/mmc (194)
III PDF file 75-2360, structure-Rhombohedral, space group-R3m (166)
IV PDF file 82-1399, structure- Rhombohedral, space group-R3c (167)
V PDF file 04-0836, structure-Cubic, space group-Fm3m (225)

The lattice spacings corresponding to these peaks and humps appeared to match with those of β-CuAlO₂ among various combinations of Cu, Al and O as listed in Table 4-1. The other possible phases in the film were cubic Cu, hexagonal CuAlO₂ (P6₃/mmc), rhombohedral CuAlO₂ (R3m), rhombohedral Al₂O₃. To further determine the phase, high resolution TEM was employed.

Figure 4-3 shows the diffraction pattern and the high-resolution TEM image of the sample. The lattice spacings corresponding to the rings in the diffraction pattern were
determined with the camera constant of the equipment and the measurement of the ring radii from the negative.\(^5\) The lattice spacings deduced from the rings were compared with the powder diffraction file (PDF)\(^6\) of various copper aluminum oxides copper oxides, and aluminum oxide.

![Electron diffraction pattern and high-resolution transmission electron microscopic (TEM) image](image)

**Figure 4-3** Electron diffraction pattern (left) and high-resolution transmission electron microscopic (TEM) image (right) of the Cu–Al–O film prepared from acac precursors. TEM has a high tension of 300kV.

It was found that the rings could be related to several copper or aluminum oxides, and the corresponding lattice spacings were listed in Table 4-2. First of all, no ring could match the lattice spacings of copper, so metal copper was excluded. In the TEM experiments, the high-energy electrons hit the sample, thus the sample is heated and disturbed by the electron bombardment. However, even when the sample inside the TEM chamber is heated, metal copper will not be oxidized because of the ultra high vacuum in the chamber. Now no ring could match the lattice spacings of copper, it can
be said that no metal copper crystal existed in the film. It was also noticed that no low-index planes of hexagonal CuAlO$_2$ and CuAl$_2$O$_4$ could match the rings in the diffraction pattern. Therefore, they were further excluded. The lattice spacings of β-CuAlO$_2$ and rhombohedral CuAlO$_2$ could fit most of the lattice spacings calculated from diffraction rings. However, according to the PDF, the phase of β-CuAlO$_2$ decomposes at a temperature above 360°C. For nano-structured films, this temperature can be even lower. Therefore at elevated temperature, β-CuAlO$_2$ might not exist. Now rhombohedral CuAlO$_2$ was possibly the only main phase observed by TEM. Cubic Cu$_2$O might exist because it matched small lattice spacings not being matched by rhombohedral CuAlO$_2$ and it is noticed that rhombohedral CuAlO$_2$ combined with cubic Cu$_2$O could match all the rings.

Measuring the lattice spacing from the atomic-resolution TEM image (Figure 4-3) revealed 2.48±0.05Å, 2.38±0.05Å for most grains with a very few exceptions of 2.07±0.05Å. It is noticed that all crystallites were sized below 10nm. Referring to Appendix D, 2.48±0.05Å could correspond to rhombohedral CuAlO$_2$ (101), β-CuAlO$_2$, hexagonal CuAlO$_2$ (100) or cubic Cu$_2$O (111). 2.38±0.05Å coincided with rhombohedral CuAlO$_2$ (012) or rhombohedral Al$_2$O$_3$ (110) while 2.07±0.05Å could correspond to β-CuAlO$_2$, rhombohedral Al$_2$O$_3$ (113) or cubic Cu (111). Other atomic planes with smaller spacings were not observed in the TEM image due to the resolution limit of the equipment. Since some of the phase candidates were excluded by the previous analysis, these grains could correspond to rhombohedral CuAlO$_2$, cubic Cu$_2$O and rhombohedral Al$_2$O$_3$. 

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Table 4-2 The lattice spacings (LS) (Å) deduced from the rings in the electron diffraction pattern (DP) (Figure 4-2) of the Cu-Al-O film and the lattice spacings (LS) of relevant materials (e.g. CuAlO₂, Cu₂O and CuAl₂O₄) from PDF, (LS data in bold are very close to experimental data).
EDX results showed that the ratio of Cu to Al was close to the atomic ratio of Cu and Al in CuAlO$_2$, further confirming that the main phase in the film was CuAlO$_2$. Since EDX is known to be a semi-qualitative analysis tool, other methods were employed to quantify the film composition. Such as XPS and Auger techniques. XPS showed mainly Cu$^+$ 2$p_{3/2}$ peak. Normally, the 2$p_{3/2}$ binding energy of Cu$^+$ is from 932.5eV to 932.7eV in different compounds. Due to the resolution limit and the lack of the accurate binding energy value of Cu$^+$ in CuAlO$_2$, it is impossible to determine if ion Cu$^+$ was from Cu$_2$O or CuAlO$_2$. It is also impossible to determine by the Auger technique due to same reasons. Similarly it was difficult to find out if the ion Al$^{3+}$ came from Al$_2$O$_3$ or CuAlO$_2$.

In a comprehensive assessment of the data, it appears that the main phase observed by XRD was $\beta$-CuAlO$_2$ and the phases revealed by TEM were possibly rhombohedral CuAlO$_2$, cubic Cu$_2$O and rhombohedral Al$_2$O$_3$.

Here comes a problem that TEM did not reveal most of the lattice spacings observed by XRD. One sound reason is as mentioned above: $\beta$-CuAlO$_2$ phase found by XRD might have decomposed. Gessner$^7$ first pointed out that $\beta$-CuAlO$_2$ decomposed at above 360$^\circ$C without stating the products. In the TEM chamber, the temperature of the sample can be far above this due to the strike of the electron beams. As normally thought, $\beta$-CuAlO$_2$ decomposes to Cu$_2$O and Al$_2$O$_3$. Is it possible that $\beta$-CuAlO$_2$ converted to rhombohedral CuAlO$_2$ under the bombardment of high-energy electron beams? This question will be answered in the next section.

Another problem is that the lattice spacings observed by TEM were not shown in XRD. This could be due to the different observation angles of these two techniques.
and the phases in the film had preferred orientations. In XRD, the incidence angle of X-ray is 1° but in TEM the electron beam strikes the film from upside. Thus if one phase in the film had a preferred orientation, XRD and electron diffraction TEM might see different planes.

Figure 4-4 (a) The optical transmission spectrum of the Cu-Al-O film and (b) a plot of \((\alpha h\nu)^2\) against \(h\nu\) for the determination of optical bandgap. The bandgap is estimated to be 3.75 eV.
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Figure 4-4(a) shows the optical transmittance as a function of wavelength for this PECVD-grown film, and Figure 4-4(b) displays a plot of \((\alpha h\nu)^2\) against \(h\nu\) for the determination of the optical bandgap, where \(\alpha\) is the absorption coefficient and \(h\nu\) is the photon energy. The transmittance of the film was 12-52% in the UV-visible range. The direct optical bandgap was estimated to be 3.75eV from the extrapolation of \((\alpha h\nu)^2\) to the \(h\nu\) axis (Figure 4-4(b)), which was higher than the 3.5eV for laser-ablation prepared CuAlO$_2$ and the 2.1eV for Cu$_2$O. To estimate the possible experimental error for this bandgap value, an exaggeratedly large sample-thickness variation (±20%) was assumed in calculating \(\alpha\) but the resulted bandgap deviation was less than 0.05eV.

This indicated that the optical bandgap of this film was truly wider. Quantum confinement may be the cause of this wider bandgap because the exciton confinement in semiconductor nanocrystals leads to the development of discrete, excited electronic states with higher oscillator strength and to bandgaps that increase as an inverse function of crystallite size.$^{10,11}$

It is expected that a semiconductor with larger optical bandgap may have a higher transmittance, but the transmittance obtained appears even slightly lower than that of the laser-ablation prepared CuAlO$_2$. This phenomenon may be attributed to the scattering and absorption of photons by grain boundaries and impurity particles in the film and the degradation of the optical properties of the material due to the surface states of semiconductor nanocrystals.$^{12}$

The Hall measurement using the Van der Pauw configuration revealed a sheet Hall coefficient, mobility and carrier concentration of $+1.0 \text{m}^2\cdot\text{C}^{-1}$, $0.5\text{cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ and...

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2.6×10^{19}\text{cm}^{-3}$, respectively. The positive sign of the Hall coefficient indicated a \textit{p}-type conduction, and this \textit{p}-type nature was further confirmed by the positive voltage at the cold end in the Seebeck measurement. The \textit{p}-type conductivity of the Cu-Al-O film was found to be 2.0S·cm$^{-1}$, much higher than 0.95×10^{-1}S·cm$^{-1}$ of the laser-ablation prepared CuAlO$_2$\textsuperscript{8} and that of 10^{-9}S·cm$^{-1}$ of Cu$_2$O$^9$. The temperature dependence of resistance of the film is shown in Figure 4-5. A straight line was observed in the Arrhenius plot, which showed typical semiconductor behavior and the activation energy was found to be 0.12eV which was smaller than 0.2eV of the laser-ablation prepared CuAlO$_2$.\textsuperscript{8} This smaller activation energy for the positive holes may be the main reason of the higher conductivity for the present film.

![Figure 4-5](image-url)  

Figure 4-5 The natural logarithm of the inverse of the resistance as a function of temperature for the Cu-Al-O film. The unit of resistance $R$ is ohm. The activation energy estimated is 0.12eV.

The mobility of the present film was similar to that (10.4cm$^2$·V$^{-1}$·s$^{-1}$) of Kawazoe \textit{et al.}\textsuperscript{8} (In a later publication they announced that the mobility was actually smaller than $P$-type transparent conducting Cu-Al-O thin films 59
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1cm²·V⁻¹·s⁻¹)¹³. This small mobility of the present film may be due to the small grain size and high density of grain boundaries in the film. Alivisatos¹² indicated that electrical transport depended strongly on grain size mainly because of the large variation in energy required to add or remove charges on a nanocrystal. On the other hand, the carrier concentration was 2 orders higher than the value of 1.3×10¹⁷ cm⁻³ for the laser-ablation prepared CuAlO₂, which is possibly due to the smaller activation energy, nanoscale effect and the film-growth technique employed.

However, similar to previous researchers,⁸,¹⁴ the mechanism regarding the p-type conduction is still not clear. Kawazoe et al.¹⁴ suspected that excess oxygen might probably be the cause of p-type conduction, but they lacked experimental evidence and admitted that the origin of the positive ions was not clear for CuAlO₂ as well as the succeeding p-type SrCu₂O₂ (conductivity: 4.8×10⁻² S·cm⁻¹). Porat and Riess¹⁵ proposed that the origin of the holes in Cu₂₋yO could be copper vacancies and oxygen interstitials. Until now, this is the most acceptable theory.

The co-doping theory¹⁶ may also be useful in understanding the large p-type conductivity and the small activation energy for the positive holes of the present film. Yoshida et al.¹⁶,¹⁷ employed the co-doping theory to interpret the p-type conduction of a few wide-bandgap semiconductors such as GaN, AlN, ZnSe and ZnO. Their calculation revealed that the simultaneous co-doping of n-type and p-type dopants led to the decrease in the Medelung energy compared with the doping with acceptors alone. Therefore, the p-type dopant incorporation was enhanced. For CuAlO₂, if similar to Cu₂O, the singly charged copper vacancy and the doubly charged oxygen interstitial can be the origins of p-type conductivity,¹⁵ a small amount of Cu²⁺ ions
(shown in a later part) can act like \( n \)-type co-dopants. The strong interaction between the reactive co-dopants and \( p \)-type dopants might have enhanced the incorporation of \( p \)-type dopants and lowered the acceptor levels. However, the co-doping theory still lacks evidence and a combination of theoretical and experimental work on different systems is still needed for a full understanding of \( p \)-type conduction.

### 4.3.2 The effect of growth temperature on the properties of Cu-Al-O films

It is important to investigate the effect of growth temperature on the properties of the films. In this part the Cu-Al-O films were grown under the following conditions: the \( \text{O}_2 \) flow rate at 8sccm, the \( \text{Ar} \) flow rate at 30sccm, the working pressure at 150mTorr and the plasma power at 100W. The substrate temperature was varied over the range 630-800°C.

Figure 4-6 shows the growth rate of the films as a function of the substrate temperature. The results showed that the film growth rate increased exponentially from 1.3nm/min to 2.0nm/min when the substrate temperature rose from 630°C to 800°C. This indicated that film growth obeyed the Arrhenius law\(^{18} \)

\[
\gamma_{\text{grow}} = A \exp \left(-\frac{E_A}{RT}\right) \quad (4-1)
\]

where \( \gamma_{\text{grow}} \) is the growth rate, \( E_A \) is the apparent activation energy, \( R \) is the gas constant, \( A \) is a constant and \( T \) is the growth temperature.

In Figure 4-6, the growth rate was exponential with the inverse of temperature when the error in thickness measurement was taken into account. In this temperature region, the growth rate is limited by chemical kinetics, uniform film thickness can be achieved by minimizing temperature fluctuation.\(^{18} \) This is the regime desired in hot-
wall LPCVD reactors. In the reaction process, the present reactor system was quite similar to the LPCVD reactors so this temperature region was applied in this work.

Figure 4-6 Growth rate is plotted on a natural logarithm scale against the inverse of substrate temperature $T_{sub}$ of the Cu-Al-O films prepared from acac precursors.

Figure 4-7 XRD of as-deposited films from acac precursors grown at different temperatures.
XRD results were similar to those in section 4.3.1 (see Figure 4-7). Peaks observed here were at about 43.36° (2.088Å) and 50.45° (1.810Å). There was one more peak at 53.54° (1.712Å), which was the additional proof of the existence of β-CuAlO₂. No other copper or aluminum related compounds were found to match all these lattice spacings. It can be seen that all the peaks here corresponded to metastable β-CuAlO₂.

The films were annealed in the RHF 1400 Carbolite furnace at 350°C for 5 minutes in air. Figure 4-8 shows the XRD spectra of the annealed films, where all the peaks mentioned above disappeared and three new peaks appeared. The three new peaks are at 36.40° (2.469Å), 42.30° (2.138Å) and 61.36° (1.512Å). This change is because of the disappearance of the phase β-CuAlO₂. Although annealing was set at 350°C, the actual temperature of the furnace fluctuated around this point and overheating would result in the transition from β-CuAlO₂ into other phases.

Figure 4-8 XRD spectra of 350°C annealed films, which were deposited at different temperatures from acac precursors.
Cubic $\text{Cu}_2\text{O}$ could match all the peaks perfectly and CuO matched the experimental results with some deviations. Rhombohedral $\text{CuAlO}_2$ could only match two of three peaks. The result of XPS (shown later) indicated that the main valence of copper in the films was +1, thus CuO could not be dominant.

Next, let us consider the problem whether $\beta$-$\text{CuAlO}_2$ decomposes to $\text{Cu}_2\text{O}$ or converts to rhombohedral $\text{CuAlO}_2$ at high temperature. If the former reaction happened, the phase seen by XRD in the annealed films (Figure 4-8) was then $\text{Cu}_2\text{O}$; if the latter transition happened, the phases observed by XRD could be rhombohedral $\text{CuAlO}_2$ and cubic $\text{Cu}_2\text{O}$. In the latter case, it is difficult to explain why $\text{Cu}_2\text{O}$ was not observed by XRD before annealing. Because the annealing temperature was not high enough to promote the growth of grain so grain size would not change much after the annealing. Thus it suggested that $\beta$-$\text{CuAlO}_2$ decomposed to $\text{Cu}_2\text{O}$ and $\text{Al}_2\text{O}_3$, but $\text{Al}_2\text{O}_3$ is often in amorphous state and cannot be seen by XRD.

As discussed in section 4.3.1, rhombohedral $\text{CuAlO}_2$ in the as-deposited films could have preferred orientation, which resulted in the inability of XRD to detect it. After annealing, similar to the phase of cubic $\text{Cu}_2\text{O}$, the phase of rhombohedral $\text{CuAlO}_2$ would not have much change so it was still not able to be detected by XRD.

The conclusion from all the above analysis is that the as-deposited films contained mainly $\beta$-$\text{CuAlO}_2$ and rhombohedral $\text{CuAlO}_2$ while $\beta$-$\text{CuAlO}_2$ was observed by XRD and rhombohedral $\text{CuAlO}_2$ was seen by TEM. After annealing at 350°C, the films mainly contained rhombohedral $\text{CuAlO}_2$, $\text{Cu}_2\text{O}$ and $\text{Al}_2\text{O}_3$, while only $\text{Cu}_2\text{O}$ was observed by XRD.
Figure 4-9 SEM micrographs of as-deposited films grown at different temperatures of (a) 700°C, (b) 750°C and (c) 800°C.
SEM pictures of the as-deposited films are shown in Figure 4-9. It can be seen clearly that the film grown at 700°C had a loose structure with a small particle size of about 25nm. The films deposited at a higher temperature (750°C) showed a similar structure with a larger particle size of about 40-50nm. At the growth temperature of 800°C, the films looked more compact and the particle sizes reached about 50-70nm. It is apparent that the grain size of the film increased as the growth temperature increased, which can be understood by a higher mobility of atoms at a higher growth temperature.

The variations of the optical transmittance of the as-deposited and annealed films are shown in Figure 4-10, which was normalized to the film thickness of 100nm. The transmittance in the region 300 to 1100nm of the as-deposited film grown at 700°C was from 24.8% to 69.3%, and those of the films grown at 750°C and 800°C were from 34.3% to 75.2%. It is easily seen that after annealing the transmittance of every
sample was improved by about 5-15%. After annealing, the films deposited at 750°C and 800°C reached a high transmittance from 43.7% to 80.5%.

The reasons for the improvement in the film transmittance are not very clear yet. Phase transition can be a reason. In addition, if it is considered that a small amount of impurities existing in the film, the improvement of transmittance can partly be due to the disappearance of these scattering centers upon annealing.

The Hall effect measurement was found not suitable for the determination of the type of conductivity for these samples due to several reasons, which will be discussed later. Therefore, the Seebeck effect was employed to test the type of the conductivity. The results showed that all films had a stable $p$-type characteristic. The resistivities of the as-deposited and annealed films are listed in Table 4-3. It is found that the film had a lower resistivity when it was prepared at a higher growth temperature. As indicated previously, the grain size increased with the increase of the substrate temperature. Consequently, the grain boundary potential decreased leading to an increase in mobility and a decrease in resistivity.

Table 4-3 Resistivities of the as-deposited and annealed films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Before annealing (Ω⋅cm)</th>
<th>After annealing (Ω⋅cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Grown at 700°C</td>
<td>35.1</td>
<td>99.1</td>
</tr>
<tr>
<td>Grown at 750°C</td>
<td>20.9</td>
<td>42.3</td>
</tr>
<tr>
<td>Grown at 800°C</td>
<td>3.7</td>
<td>5.2</td>
</tr>
</tbody>
</table>

After annealing, the trend of resistivity remained the same but the resistivity increased for each film. The effects of post-deposition annealing are complex and several
phenomena may take part in the observed changes. These include: (a) crystallinity of the film may improve, thereby the grain size is increased; (b) chemisorption and desorption of oxygen from the grain boundaries may occur; (c) phase change may happen. Phenomenon (a) may take place in cases where the deposition temperature is much less than the annealing temperature. Here the annealing temperature (350°C) is much lower than the deposition temperature thus the crystallinity could not be improved. The concentration of oxygen states at the grain boundaries relative to the ambient oxygen pressure over the film determines whether chemisorption or desorption takes place to reach an equilibrium.

![Graph showing Optical Bandgap versus Substrate Temperature](image)

Figure 4-11 Optical bandgap versus substrate temperature for the as-deposited (■) and annealed films (●).

In the process of deposition, defects like vacancies and interstitials could be formed. Especially the grain boundaries could trap a significant amount of interstitial oxygen. Once the film was heated, these defects acquired extra energy to move. As mentioned in the previous section, oxygen interstitials and copper vacancies may cause the $p$-type...
conduction of the copper aluminum oxide films. Annealing led to the decrease of the concentration of these defects, which resulted in the increase of resistivity.

The variations of the direct optical bandgap of the films before and after annealing versus growth temperature are plotted in Figure 4-12. It is seen that the bandgap of the film decreased with the increase of the growth temperature. For instance, the bandgap of the as-deposited films had values of 3.93eV and 3.77eV when they were deposited at 630°C and 800°C, respectively. The annealed films also had a similar trend with the bandgap decreasing from 3.9 to 3.79eV when the growth temperature rose from 700 to 800°C. For one film, the values of the bandgap before and after annealing can be regarded as the same if the error is considered. The optical bandgap will be discussed in more details in section 4.4.3.

In the XPS experiment, the Mg Kα monochromatized source (1253.6eV) was used and the pressure in the analysis chamber was $5 \times 10^{-9}$Torr. The films were first sputtered for 30 minutes with a beam current of 0.2µA to remove the contamination from the surface. The different spectra of C1s and Cu2p3/2 before and after the sputter-cleaning are shown in Figure 4-13 (Cu2p3/2 spectrum is plotted after calibration by taking the C1s peak as 284.8eV). Before sputtering, spectrum C1s was quite intense but spectrum Cu2p3/2 was weak, and another peak existed around 934.7eV which may possibly be from contamination such as Cu(acac)$_2$. After sputtering, the peak position of C1s remained nearly the same and the intensity of C1s only decreased a little bit, which meant that the film contained carbon contamination inside the film. However, the peak at 932.6eV of Cu2p3/2 became much sharper and more intense, which implied that the Cu$^+$ ions dominated inside the film.
In XPS, the core level binding energy of an element changes with its valence. From the XPS handbook, the binding energy of Cu$2p_{3/2}$ peaks of Cu$_2$O is around 932.7eV and that of CuO is about 933.8eV, which means that copper with valence +2 has higher binding energy of 2p electrons.

Figure 4-12 A comparison of C1s and Cu$2p_{3/2}$ spectra before and after sputter-cleaning.
Due to the static charge problem, the peak observed normally deviates from the true value by a few eVs. Therefore, the C1\textsubscript{s} line from adventitious hydrocarbon that is nearly always present on samples is used for static charge calibration. However, it may not be used after ion beam etching for it is still not sure whether a reproducible line position exists for C remaining on the surface after ion beam etching\textsuperscript{25}. Another method, by using a modified Auger parameter, could be employed to determine the valence of copper even with the effect of static charge\textsuperscript{25}. The Auger parameter $\alpha$ is defined as the difference in kinetic energy (KE) between the Auger (A) and photoelectron (P) lines

$$\alpha = KE_A - KE_P$$  \hspace{1cm} (4-2)

or as the difference in binding energy (BE) between the photoelectron and Auger lines. This difference can be accurately determined because static charge corrections are cancelled with all kinetic and binding energies referenced to the Fermi level (zero binding energy by definition). The kinetic energy is given by

$$KE = h\nu - BE$$  \hspace{1cm} (4-3)

here $h\nu$ is the photon energy (1253.6eV). Substituting $KE_P$ by $h\nu - BE_P$ into Eq. 4-2,

$$KE_A + BE_P = h\nu + \alpha$$  \hspace{1cm} (4-4)

The sum of the kinetic energy of the Auger line and the binding energy of the photoelectric line equals to the Auger parameter plus the photon energy, which is called the Modified Auger parameter. This Modified Auger parameter is independent of the static charge\textsuperscript{25}. This method can be very useful for identifying chemical states of some multi-valence element when several valences do not exist at the same time. An element has similar binding energies in different compounds when it has the same
valence. Copper has three chemical states: Cu$^0$, Cu$^+$ and Cu$^{2+}$, whose core level photoelectron lines and Auger lines are at different positions (Table 4-4). The modified Auger parameters for Cu$^0$, Cu$^+$ and Cu$^{2+}$ are also listed in the table.

Table 4-4 Binding energies of Cu$2p_{3/2}$ and kinetic energies of CuLMM for different chemical states of copper (All the data are from same research group). $^{25}$ BE$_p$, KE$_A$, $h\nu$, $\alpha$ are binding energy of photoelectron, kinetic energy of Auger electron, photon energy and Auger parameter, respectively.

<table>
<thead>
<tr>
<th></th>
<th>Cu$^0$</th>
<th>Cu$^+$</th>
<th>Cu$^{2+}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>BE$<em>p$ (Cu$2p</em>{3/2}$)</td>
<td>932.6eV</td>
<td>932.5eV</td>
<td>933.7–936.1eV</td>
</tr>
<tr>
<td>KE$_A$(CuLMM)</td>
<td>918.6eV</td>
<td>915.0–917.2eV</td>
<td>916.0–918.1eV</td>
</tr>
<tr>
<td>$h\nu + \alpha$</td>
<td>1851.2eV</td>
<td>1847.5–1849.7eV</td>
<td>1850.8–1852.6eV</td>
</tr>
</tbody>
</table>

Although the TEM result in section 4.3.1 indicated that no metal copper was in the film, to make sure that metal copper does not confuse the XPS analysis (Cu$^0$ and Cu$^+$ have close binding energies), the XPS spectra of Cu$2p_{3/2}$ and CuLMM (no calibration was applied) of the as-deposited film grown at 800$^\circ$C are shown in Figure 4-13. These spectra were taken before sputter-cleaning thus the signal-noise ratio was not so good. It is clearly seen that in both figures, the peaks contained more than one component, possibly two components. The possible components of the peaks are listed in Table 4-5. The modified Auger parameters of different combinations are also summarized in the table. The modified Auger parameter for Cu$^+$ (1847.2–1848.0eV) can match the value listed in Table 4-4, and so can Cu$^{2+}$ (1850.6–1851.4eV). However, the modified Auger parameter for Cu$^0$ (1848.9–1849.3eV) has large deviation from the value given by the reference (1851.2eV). This is an additional proof that no metal
copper existed in the as-deposited films and the peaks obtained by XRD were from Cu-Al-O compounds.

Figure 4-13 XPS spectra of Cu2$p_{3/2}$ and CuLMM of the film grown at 800°C.
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The XPS Cu2p3/2 spectra (calibrated) of annealed films with comparison of Cu2O and CuO are presented in Figure 4-14. A comparison of the spectra obviously shows that the main copper component in the films was Cu+.

Table 4-5 Experimental values of KEA (first row) and BEp (first column), and their sums (modified Auger parameters). The possible valences for each peak are written in the bracket below the peak position. The modified Auger parameters in bold match the values given by reference.25

<table>
<thead>
<tr>
<th>BEp</th>
<th>KEA</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>936.0±0.2eV (Cu0, Cu+)</td>
<td>913.3±0.2eV (Cu0, Cu2+)</td>
<td>911.6±0.2eV (Cu+)</td>
<td></td>
</tr>
<tr>
<td>937.7±0.2eV (Cu2+)</td>
<td>1848.9–1849.3eV</td>
<td>1847.2–1848.0eV</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1850.6–1851.4eV</td>
<td>Not applicable</td>
<td></td>
</tr>
</tbody>
</table>

This can also be confirmed from the Auger spectra of copper LMM peak (shown in Figure 4-15). Although the Auger peak was broader than the core level peak and

Figure 4-14 XPS 2p3/2 spectra of copper of the 350°C annealed films compared with the spectra of Cu2O and CuO, temperatures shown in the figure are growth temperatures.

P-type transparent conducting Cu-Al-O thin films