# SYNTHESIS OF CuAlO<sub>2</sub> THIN FILMS BY PULSED LASER DEPOSITION

by

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# Abstract

This work presents a procedure that has never been published before for producing transparent CuAlO<sub>2</sub> thin films. Pulsed laser deposition was used to fabricate films composed of a mixture of Cu<sub>2</sub>O and Al<sub>2</sub>O<sub>3</sub> in a proportion stoichiometric to CuAlO<sub>2</sub>. Samples were then heat treated using a system designed for rapid thermal annealing in order to achieve complete reaction of the two compounds. It was found that deposited films require a heating ramp rising from room temperature up to 1050°C in the order of seconds, and dwell times at this temperature in the order of minutes. Films fabricated by this procedure are single-phase CuAlO<sub>2</sub>, and have conductivities of up to 0.017 S/cm. The material was found to have grown epitaxially oriented on sapphire substrates by off-plane XRD analysis, and a suitable model for this interface has been proposed.

# Resumen

Este trabajo presenta un procedimiento para producir películas delgadas y transparentes de  $CuAlO_2$  que no ha sido publicado anteriormente. Se utilizó deposición por láser pulsado para fabricar películas de  $Cu_2O$  y  $Al_2O_3$  en una mezcla estequiométrica con respecto a  $CuAlO_2$ . Las muestras luego fueron sometidas a tratamiento térmico usando un sistema diseñado para calentamiento rápido a fin de lograr la reacción completa de los dos compuestos. Se encontró que las películas depositadas requieren ser sometidas a una rampa de calentamiento ascendente desde temperatura ambiente hasta  $1050^{\circ}C$  en el orden de segundos y tiempos de recocido a esta temperatura del orden de minutos. Las películas fabricadas mediante este procedimiento resultan en  $CuAlO_2$  en fase pura y tienen conductividades de hasta 0.017 S/cm. Se encontró que el material creció orientado epitaxialmente sobre substratos de zafiro mediante análisis de DRX fuera del plano y se propuso un modelo adecuado para esta interfase.

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# Dedicatory

My deepest gratitude goes first and foremost to my family.

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# Table of Contents

Abst	tract	<i>ii</i>
Resu	ımen	<i>iii</i>
Dedi	icatory	vi
Ackr	nowledgements	vii
Tabl	le of Contents	viii
Figu	ıre List	<i>x</i>
Tabl	le List	xiii
<i>I</i> .	Introduction	1
1.	<b>Research Interest in CuAlO<sub>2</sub></b> Molecular Structure of CuAlO <sub>2</sub> P-type conductivity of CuAlO <sub>2</sub>	
2.	<b>Previous Works</b> CuAlO <sub>2</sub> Growth by PLD. CuAlO <sub>2</sub> Growth by Reactive Magnetron Sputtering followed by RTA	<b></b>
3.	Phase Diagrams featuring CuAlO <sub>2</sub>	
II.	Methodology	
4.	Pulsed Laser Deposition         Excimer Laser as beam source.         Deposition Atmosphere         Laser Ablation         Nucleation and Film Growth         PLD System Setup	<b>19</b> 19 20 21 22 25
5.	XRD Technique X-Ray Production Basics X-Ray Diffraction Basics	<b>28</b> 
6.	Electrical Measurements Measuring Resistivity: Van der Pauw Method Hardware Setup Software Setup Contact preparation procedure	<b>32</b> 32 36 39 40
7.	Target PreparationProcedure #1: Corundum(Al2O3) and Tenorite(CuO)Procedure #2: Corundum(Al2O3) and Cuprite(Cu2O)	<b>42</b> 42 46
8.	Sample Annealing Procedures In-situ Annealing Ex-situ Annealing Rapid Thermal Annealing – Preliminary Justification Rapid Thermal Annealing – System Setup Rapid Thermal Annealing – System Characterization	<b>50</b> 50 50 50 52 52 52 52 57

III.	Results and Discussion	
9.	. Crystal structure orientation for CuAlO <sub>2</sub> in Sapphire	60
	Substrate Structure Analysis	
	CuAlO <sub>2</sub> Plane Structure Analysis	
	referential Glowin for CuAlO <sub>2</sub> // (e-cut Sappline)	
1	0. Precursor Depositions	
	As-Deposited Phase Purity by PLD	
	Precursor Types – Resulting Compounds	
	A-ray-Amorphous Precursor	
	$Cuprite (Cu_{2}O) Precursor$	
	Deposition on Glass Substrates	71
4		
1.	I. Annealing the Samples	
	Establishing the Annealing Temperature	
	Effects from the Annealing Dutation	
	Remarks on the formation of $CuAlO_2$ from $CuO$ and $Al_2O_2$	
	Final deposition duration and conditions.	
	Remarks on plausible explanation for CuAl <sub>2</sub> O <sub>4</sub> persistence	
13	2 Electrical Measurements	91
	Resistivity Measurements	
	Hall Effect Measurements	
13	3 D Scan Technique: Confirming enitavial growth	93
1,	$\Phi$ Scan: Experimental results for Sapphire	95
	$\Phi$ Scan: Experimental results for the CuAlO <sub>2</sub> film	
14	4. Geometry of the CuAlO <sub>2</sub> // Sapphire interface	
IV.	Conclusion	102
<b>_</b> / •	Future works	
Pofe	24014.000	105
neje		

# Figure List

Figure 1.1 – Absorption coefficient for thin films (0.185µm), and bulk sample (47.9 µm)	2
Figure 1.2 – Absorption coefficient as measured with a 11.3µm thick sample. <sup>9</sup>	3
Figure 1.3 – Generic structure for delafossites. M <sup>1+</sup> and M <sup>3+</sup> represent the monovalent and trivalent cations respectively, while O <sup>2-</sup> is oxygen. The scale, relative to the lattice	
parameter 'c', of the hexagonal conventional cell, is shown on the left. Image	
adapted from publication.	4
Figure 1.4 – An electronic band gap designed for transparency. Photons of visible light, between 2.1 and 3.1 eV, do not have enough energy to excite an electron from the valence hand to the conduction hands, and they have too much energy to excite a	
hole <sup>16</sup>	6
Figure 3.1 – Phase Diagram reported for the CuO-ALO, system <sup>36</sup>	14
Figure 3.2 – Isobaric section of ternary system $Cu_0O-Cu_0O-Al_0O_1$ at $p_{00} = 0.21$ atm. as	
presented by (A) Gadalla and White <sup>37</sup> (B) Jacob and Alcock <sup>38</sup>	16
Figure 3.3 – Isobaric section of ternary system Cu <sub>2</sub> O-CuO-Al <sub>2</sub> O <sub>3</sub> at $p_{O2} = 0.40$ atm, as	
presented by (A) Gadalla and White " (B) Jacob and Alcock "	16
Figure 4.1 – Simple growth model – Randomly stacked piles of adatoms over the substrate	•••
surface. Image adopted from reference.	23
Figure 4.2 – Visual interpretation and comparison of three growth models in thin films. Image	•
adapted from reference.	24
Figure 4.3 – Diagram of the PLD System.	25
Figure 4.4 – Stainless steel vacuum chamber with peripheral equipment	26
Figure 5.1 - A-Kay emission diagram	29
Figure 5.2 - Bragg Reflection	
Figure 5.5 - Geometry of a 0- 20 scali	
Figure 0.1 – Basic Horizontal and vertical configurations for resistance measurements	
Figure 6.2 – Graphical representation of f as a function of $R_{mn,op}/R_{no,pm}$	35
Figure 6.3 - G.M.W.® Electromagnet Model 3472-70	37
Figure 6.4 – Outline sketching the measuring process. The subpicture of the equipment depicts	
the Keithley devices with model number 2400(DC Supply), 2182 (Nanovoltmeter),	
7065/7001(Hall effect card holder) and the 6485(Picoammeter) Left to right, and	
top to bottom respectively.	39
Figure 6.5 – Cloverleaf geometry suggested for Hall coefficient measurements	40
Figure 6.6 – Masking the samples. (Not drawn to scale)	41
Figure 7.1 – Mechanical Grounding/Pre-Mixing Equipment	43
Figure 7.2 – Agate Pellets with Micronising Mill	43
Figure 7.3 – Solvent Evaporation	44
Figure 7.4 – XRD Analysis, CuAlO <sub>2</sub> pellet (from CuO+Al <sub>2</sub> O <sub>3</sub> - first heating)	45
Figure 7.5 – XRD Analysis, CuAlO <sub>2</sub> pellet (from CuO+Al <sub>2</sub> O <sub>3</sub> - second heating)	46
Figure 7.6 – XRD Analysis, CuAlO <sub>2</sub> pellet (from Cu <sub>2</sub> O+Al <sub>2</sub> O <sub>3</sub> - first heating)	48
Figure 7.7 – XRD Analysis, CuAlO <sub>2</sub> Pellet (from Cu <sub>2</sub> O+Al <sub>2</sub> O <sub>3</sub> - second heating)	49
Figure 8.1 – Cooling rate for furnace after heating elements are turned off	51
Figure 8.2 – Furnace Model F4/918. Arrow indicates air vent.	
Figure 8.5 – Fabricated Sample Holder from two view points.	
Figure 8.4 – Diagram representing the goals of the system, and uses lation of the stemper motor.	
Figure 8.6 Distures illustrating the DTA setup	
Figure 8.7 Abrunt rise in temperature as measured trough the linear noth of the second	
holder. The furnace was kent at the controlled temperature of 1150°C	57
Figure 8.8 – Temperature rise in the process as measured by a thermocounle on the sample	
holder. The heating step rate for this case is 3ms/step	58

Figure 8.9 – Temperature rise as measured when the heating step rate is slowed down to	59
Eigure 8.10 Temperature drep as measured when the cooling step rate is 3 ms/step	
Figure 0.1 - Left Image (0001) plane for a ALO or "a out compliant". The other lefting	
constant (not depicted for clarity) is c=12.9929Å directed toward ±z	60
Figure 9.2 – <i>Right Image</i> - α-Al <sub>2</sub> O <sub>3</sub> Hexagonal unit cell. Filled circles represent Al atoms, and open circles represent O atoms.	60
Figure 9.3 – Hexagonal unit cell for CuAlO <sub>2</sub> (Image adapted from publication). The layers marked as (*) are called the edge sharing layers, and the layer marked (†) will be used in a future reference.	
Figure 9.4 – One particular case of unit cell conversion. Depicted in (A) are rhombohedral	()
$(001)_R$ planes, now equivalent to (B) nexagonal $(0111)_H$ planes	
Figure 9.5 – CuAlO <sub>2</sub> phase pure sample. Peaks marked *Kα and *Kβ are due to the (006) plane of the sapphire substrate, diffracting from the main and secondary wavelength emissions for Cu.	63
Figure 10.1 – Sample deposited at room temperature. Peaks marked as * are from the samphire substrate	66
Figure 10.2 – Annealed film resulting from an amorphous precursor. (T <sub>anneal</sub> =1,050°C, and an anneal time of 2 minutes by RTA)	67
Figure 10.3 – Published works featuring samples with annealed amorphous precursors: Stauber et. al (top), Neumann et. al. (bottom). Peaks marked as § are from	67
Figure 10.4 – Results obtained by using the same conditions reported by Vanagi et. al	
Figure 10.5 – Cuprite precursor with observed peaks of (110), (111), (200), and Al $O_3$ in (018),	
Figure 10.6 - Cuprite precursor with observed peaks of (110), (111), and $A_2O_3$ in (018)	
Figure 10.7 - Cuprite precursor with observed peaks of (111), (200), and no peaks of $A_2O_2$	
Figure 10.8 – As deposited film on a SiO <sub>2</sub> substrate	72
Figure 10.9 – Subsequent annealings of a sample deposited on SiO <sub>2</sub>	72
Figure 11.1 – Sample annealed at 1,200°C for 3h. Visual inspection seems to corroborate substantial sample evaporation	74
Figure 11.2 – XRD results for the ex-situ annealing experiments performed at temperatures	75
Figure 11.3 – Phase diagram for $p_{02} = 0.21$ atm (air) presented by Jacob and Alcock, with a featured highlight over the region tested for compound equilibrium by ex-situ anneals.	
Figure 11.4 – Comparison of two samples annealed for 1.5h, and 3h, at 1050°C.	79
Figure 11.5 – Comparison of samples annealed for 1.5h at 1050°C, but using two furnaces with	
different thermal masses, resulting in extended heating and cooling ramps for the heavier of the set.	
Figure 11.6 – XRD Result from rapidly cooling a sample by removing it from the furnace while	
onerating at the highest temperature set-point of 1050°C	81
Figure 11.7 – Resulting XRD for samples heated at increasing rates.	
Figure 11.8 – Amplification of the curve depicted as "12ms/step" in Figure 11.7.	
Figure 11.9 – Subsequent re-anneals, 2minutes each, at temperatures of 1050°C for the first one and 1100°C for the others	85
Figure 11.10 – Schematic for $CuAlO_2$ growth. Model suggested by Gonzalez et. al. Picture	
auapted from publication.	06
Figure 11.11 – samples annealed at $1050^{\circ}$ , and at different anneal dwell times	
Figure 13.1 - P Orientation of the substrate	
Figure 15.2 - $\alpha$ -Al <sub>2</sub> U <sub>3</sub> oriented corundum, (sapphire) planes	
Figure 13.5 – Standard $\theta$ -2 $\theta$ scan aligned around multiples of the (001) plane (c-cut)	
Figure 13.4 – Substrate tilted at an angle of $\chi$ in order to align the (024) family of planes	
Figure 13.5 – Substrate $\Phi$ -scan	
Figure 13.6 – CuAlO <sub>2</sub> $\Phi$ -scan. Dashed lines represent the angular positions of the (024) family	
of planes measured from the sapphire substrate(Figure 13.5)	97

Figure 14.1 –	$(001) = (0001)_{\rm H}$ orientations for both sapphire and CuAlO <sub>2</sub> drawn to a relative	
S	cale with their respective lattice constants	99
Figure 14.2 – 9	Substrate surface terminated in oxygen.	.100
Figure 14.3 - 1	Hexagonal close packed layer in CuAlO <sub>2</sub> aligned with the surface of the sapphire	
SI	ubstrate	.100
Figure 14.4 - I	Diagram representing the two possible crystal orientations	.101

# Table List

Table 1.1 - List of compounds that have the delafossite structure. Adapted from publication	4
Table 1.2 - Optically measured direct band gaps for the delafossite oxides that have shown p-	
type conductivity	5
Table 2.1– Summary of methods used to fabricate CuAlO <sub>2</sub> thin films, and their resulting highest	
observed conductivity as compared to PLD, and the material in bulk	8
Table 5.1 - PDF files used troughout this work for XRD analysis, and their respective references	31
Table 6.1 – Definitions for resistance measurements in the Van der Pauw method	33
Table 6.2 – Components used for electronic measurements.	36

### I. Introduction

#### 1. Research Interest in CuAIO<sub>2</sub>

In order to continue technological development in optoelectronics, there is an endless need for solid state materials that exhibit useful electrical, and at the same time, optical properties. Up to date, regarding the available optically transparent materials, there is a marked disproportion between obtainable n-type and p-type semiconductors.

Even the simplest active electronic devices are designed based on the resulting properties of basic p-n junctions. Diverse material availability is therefore crucial in order to allow advances in transparent electronics for flat panel displays, electrodes for photovoltaic cells, electronically functional windows, transparent thin film transistors, UV light emitting diodes, and blue lasers.

The unfavorable disproportion between charge carrier type semiconductors is observed not only in Transparent Conducting Nitrides(TCN) - for example the well known n-type  $GaN^1$  it is also observed with the Transparent Conducting Oxides(TCO). Some of the TCOs that have been extensively characterized as having n-type charge carriers are ZnO, SnO<sub>2</sub>, and AgInO<sub>2</sub>:Sn<sup>2</sup>. The conductivity of these materials can also be improved by doping with n-type charge carriers. The best example for this is the already widely used Indium Tin Oxide(ITO).

Some of the p-type TCOs that have been found start with  $NiO^3$ , reported in 1993. More recent discoveries include  $ZnO:N^4$ ,  $IZO^5$ ,  $CuGaO_2^6$  and  $Cu_2SrO_2^7$ , to name a few.  $CuAlO_2$  is a promising candidate, since it can be fabricated from readily available and non-toxic oxides. For this work, the fundamental property of the material is that it also has considerable transparency in the visible spectrum. Figure 1.1 shows that the energies corresponding to optical wavelengths have a very low absorption coefficient.

It must be noted that it is much harder to produce transparent thin films, since surface defects are much more likely. When the material is in bulk, the measured absorption (plotted as a function of energy in Figure 1.2), illustrates the onset at which photon wavelengths begin to excite atoms from the valence to the conducting bands. Another particular interest in this material is that if it were doped with Fe, it might potentially produce interesting ferromagnetic properties<sup>8</sup>. This hints towards possible applications in the uncharted terrain of transparent spintronics.

The goal of this work is intended towards reliable synthesis of  $CuAlO_2$  in order to eventually produce dopable samples. Another future interest with the material might be exploring rectifying junctions by combining p-type  $CuAlO_2$  with n-type films already produced in the laboratory.



Figure 1.1 – Absorption coefficient for thin films (0.185µm), and bulk sample (47.9 µm).<sup>9</sup>



Figure 1.2 – Absorption coefficient as measured with a 11.3µm thick sample.<sup>9</sup>

#### Molecular Structure of CuAlO<sub>2</sub>

 $CuAlO_2$  belongs to the family of delafossites. This type of structure, written in general form as  $M^I M^{III} O^2$ , was discovered in 1873 by Charles Friedel with the mineral  $CuFeO_2$ . He named the structure in honor of the French crystallographer Gabriel Delafosse<sup>10</sup>. Table 1.1 lists a few known compounds that share the delafossite structure, depicted in Figure 1.3.

A univalent metal( $M^{1+}$ ), in this case  $Cu^{1+}$ , is found in two-fold linear coordination to oxygen. The trivalent cations( $M^{3+}$ ), in this case  $Al^{3+}$ , are in shared octahedra, forming sheets. The lattice parameters for CuAlO<sub>2</sub> are a = 2.856 Å, and c = 16.943 Å.



Figure 1.3 – Generic structure for delafossites. M<sup>1+</sup> and M<sup>3+</sup> represent the monovalent and trivalent cations respectively, while O<sup>2-</sup> is oxygen. The scale, relative to the lattice parameter 'c', of the hexagonal conventional cell, is shown on the left. Image adapted from publication<sup>11</sup>.

CuFeO <sub>2</sub>	AgFeO <sub>2</sub>
CuCrO <sub>2</sub>	AgCrO <sub>2</sub>
CuCoO <sub>2</sub>	AgCoO <sub>2</sub>
CuRhO <sub>2</sub>	AgRhO <sub>2</sub>
CuAlO <sub>2</sub>	AgAIO <sub>2</sub>
CuGaO <sub>2</sub>	AgGaO <sub>2</sub>
CuScO <sub>2</sub>	AgInO <sub>2</sub>
CuYO <sub>2</sub>	AgT1O <sub>2</sub>
CuLaO <sub>2</sub>	AgNiO <sub>2</sub>
CuPrO <sub>2</sub>	AgNi <sub>1/2</sub> Ti <sub>1/2</sub> O <sub>2</sub>
CuNdO <sub>2</sub>	
CuSmO <sub>2</sub>	PdCoO <sub>2</sub>
CuEuO <sub>2</sub>	PdCrO <sub>2</sub>
$CuCo_{1/2}Ti_{1/2}O_2$	PdRhO <sub>2</sub>
CuNi1/2Ti1/2O2	PtCoO <sub>2</sub>
CuCu <sub>1/2</sub> Ti <sub>1/2</sub> O <sub>2</sub>	
$CuNi_{1/2}Sn_{1/2}O_2$	
$CuFe_{1/2}V_{1/2}O_2$	

Table 1.1 – List of compounds that have the delafossite structure. Adapted from publication<sup>11</sup>.

### P-type conductivity of CuAlO<sub>2</sub>

The type of delafossites that have been found to exhibit p-type conductivity have a more specific  $CuM^{III}O_2$  structure, where  $M^{III}$  are Al, Ga, and In.  $CuAlO_2$  is of interest because as Table 1.2 shows,  $CuAlO_2$  has the lowest band gap of the three. A narrower band gap indicates that lower energy is required for charge carriers to become mobile by jumping to the conduction band.

	Band Gap (optical measurement)	Reference
CuAlO <sub>2</sub>	3.5eV	17
CuGaO <sub>2</sub>	3.6eV	6
CuInO <sub>2</sub>	3.9eV	12

 Table 1.2 - Optically measured direct band gaps for the delafossite oxides that have shown p-type conductivity.

There are several models that explain the mechanism for the p-type conductivity of CuAlO<sub>2</sub>. Benko and Koffyberg<sup>13</sup> in 1984 were the first to identify the sign of the charge carrier for bulk CuAlO<sub>2</sub>. They proposed a hole transport by hopping mechanism trough the laminar structure. Most of the reports<sup>13,14,15</sup>, propose that the p-type conductivity arises from excess oxygen placed interstitially in the lattice. The experimental basis for this statement is that conductivity is higher when oxygen content is raised in the deposition conditions.

G. Thomas<sup>16</sup> offers a more detailed explanation, starting also from the idea that ions remain trapped in interstitial sites. These  $O_2$  ions, amounts as low as  $CuAlO_{2+x}$  (where x can be 1/50,000), will bind electrons. This leaves behind empty states in the valence band which act as positive holes. A schematic of the process is shown in Figure 1.4.



Figure 1.4 – An electronic band gap designed for transparency. Photons of visible light, between 2.1 and 3.1 eV, do not have enough energy to excite an electron from the valence band to the conduction bands, and they have too much energy to excite a hole<sup>16</sup>.

Since the band gap of CuAlO<sub>2</sub> is about  $3.5 \text{eV}^{17}$ , corresponding to the blue end of the visible spectrum ~400nm, visible light photons are not energetic enough to be absorbed and excite electrons towards the conduction band. This has the effect of making the material transparent in the visible region. However, due to electron trapping by the oxygen ions, the material is also electrically conducting.

H. Kawazoe, H. Yanagi and co-workers present in their publications a much more detailed account of how they selected CuAlO<sub>2</sub> by using the theory of "Chemical Modulation of the Valence Band"(CMVB). The idea basically starts with Cu<sub>2</sub>O, which is formed since d<sup>10</sup> levels of Cu have similar energy levels to those in O - 2p. This results in covalent bonding by p-d hybridization. The non-bonding of oxygen in the coordination structure gives rise to a large dispersion in the valence band, which is another way of stating that the holes are not localized, thus behaving as a p-type semiconductor. The problem is that the band gap for this cuprous oxide is only 2.1eV. Since their goal was to find a compound which was optically transparent, they needed to find a way of suppressing the interactions between neighboring Cu and O atoms.

The delafossite  $CuAlO_2$  can be treated as a linear arrangement of O—Cu—O dumbbells, which locally are exactly the same as found in Cu<sub>2</sub>O. The delafossite on the other hand, is not a three dimensional web of dumbbells, but are instead stacked in series (along the c-axis), alternating with  $Al_3O_6$  octahedral layers, which are highly insulating. This reduces the Cu crosslinking from 3-dimensional in Cu<sub>2</sub>O, down to 2-dimensional. Now the only Cu interactions are perpendicular to the c-axis in CuAlO<sub>2</sub>. This limitation in the dispersion of the valence band results in enough widening of the band gap for successful optical transparency.

An important side effect, is that conductivity will then be inevitably anisotropic. This was confirmed experimentally by Lee et. al.<sup>18</sup> in 2001. This publication sustains that the electrical conductivity along the *ab* plane ( $\sigma_{ab}$ ) is much higher than that along the c-axis ( $\sigma_c$ ). The same study calculated that the proportion between these constants in CuAlO<sub>2</sub> is at least 25: ( $\sigma_{ab} \ge 25 \sigma_c$ ).

It has been reported<sup>11</sup> that some of the delafossites have shown an even greater anisotropy, with the proportion in conductivities typically ranging in the order of a 1000 times higher along the ab plane<sup>1</sup>.

<sup>&</sup>lt;sup>1</sup> The publication states that the conductivity is 1,000 times higher *along* the c axis, but this must be an oversight from the authors in the sentence. The discussion in the paper very clearly demonstrates that p-type conductivity is *perpendicular* to the c plane.

### 2. Previous Works

There have been numerous reports detailing procedures for preparing CuAlO<sub>2</sub> thin films, including Wet Oxidation<sup>19,20</sup>, Sol Gel<sup>21</sup>, Chemical Vapor Deposition<sup>22</sup>, DC sputtering<sup>15,23</sup>, Spray Pyrolysis<sup>24</sup>, etc. Table 2.1, which is an adaptation, updated and revised from a publication<sup>30</sup>, summarizes some of these procedures, and their respective best conductivities.

1 <sup>st</sup> Author	Ref.	Technique	Starting Materials	Substrate	Conductivity (S/cm)
Kawazoe	26				1
Yanagi	17	PLD (Pulsed Laser	CuAlO <sub>2</sub>	Sapphire	0.34
Neumann	27	Deposition)		(001)	0.3
Stauber	14				0.05
Kim	20	e-beam vapor (wet oxidation)	CuAlO <sub>2</sub>	Si (100)	0.25
Banerjee	15	DC-Sputtering	CuAlO <sub>2</sub>	glass, Si	0.39
Shahriari	25	Hydrothermal	NaAlO <sub>2,</sub> CuCl	glass	0.42
Cai	22	CVD (Chemical Vapor Deposition)	Cu(dpm) <sub>2</sub> , Al(dpm) <sub>3</sub>	quartz (001)	0.46
Tsuboi	23	DC-Reactive Sputterinng	Cu, Al	quartz	0.10
Shy	28	Reactive Magnetron Sputtering	Cu <sub>2</sub> O <sub>2</sub> Al <sub>2</sub> O <sub>3</sub>	Sapphire (001)	0.57
Youn	24	Spray Pyrolysis	Cu(NO3)2, Al(NO3)3	?	0.589
Benko	13	Sintered Body	CuAlO <sub>2</sub> (Bulk)	-	1.7 x 10 <sup>-3</sup>

# Table 2.1– Summary of methods used to fabricate CuAlO<sub>2</sub> thin films, and their resulting highest observed conductivity as compared to PLD, and the material in bulk.

The publications reporting growth by Pulsed Laser Deposition are the most relevant for this work, and will be examined in more detail.

#### CuAlO<sub>2</sub> Growth by PLD

All reports described here have certain characteristics in common, such as the type of laser used being KrF ( $\lambda = 248$ nm excimer), and base pressure for the deposition chamber being at least 7.5x10<sup>-6</sup> mTorr. All samples were deposited under O<sub>2</sub>. Argon was never included in the deposition atmosphere. For several reasons, such as lattice similarity and high fusion temperature, the substrate used in suitable samples was c-cut sapphire (Al<sub>2</sub>O<sub>3</sub>).

Kawazoe et. al. published<sup>26</sup> "P-Type electrical Conduction in transparent thin films of CuAlO2" (1997). This is the first publication that reports CuAlO<sub>2</sub> growth on thin films. The only deposition parameters mentioned in the publication, with no indication of parameter tweaking are:  $T = 700^{\circ}$ C, O<sub>2</sub> pressure of 100mTorr, laser fluence of 200mJ cm<sup>-2</sup>, and frequency of 20Hz. No information was given as to whether there was any type of annealing done to the sample, but the references in a following publication<sup>14</sup> cite a personal communication with the author suggesting an oxygen in-situ anneal. The XRD analysis reported in this publication suggests a pure phase, but film crystal structure is lacking a preferred orientation. The highest conductivity observed in the study was 1 S cm<sup>-1</sup>.

Stauber, et. al. published<sup>14</sup> **"Thin Film Growth of Transparent p-Type CuAlO<sub>2</sub>"(1999)**. This work explores different growth methods, focusing on annealing the samples. Independently of the growth temperature, the films do not show any CuAlO<sub>2</sub> diffraction peaks as deposited. A variety of substrate temperatures, oxygen pressures, distances and laser fluencies were tested. In-situ anneals of up to 3h did not help eliminate impurities. Ex-situ anneals were carried out by ramping the temperature of the furnace from 200°C to 1050°C in 1h, held for 1.5h, and gradually cooling down. Experiments with rapid quenching were performed by removing the samples from the furnace while still at 1050°C, and immediately placing them in liquid nitrogen. Diffraction peaks show that the films were predominantly

(001) textured CuAlO<sub>2</sub>, but the sample was never completely phase pure. The deposition temperature was lowered, but this results in a trade-off between surface morphology and phase purity. If the film was deposited at 100°C-200°C, the films resulted highly phase pure, but macroscopic surface defects make electronic measurements impossible. If the films were deposited in the temperature range of 700°C-950°C, trace impurities could still be observed in the XRD patterns, but films were more conductive. The optimal conditions in terms of phase purity and conductivity were carried out under high temperature 800°C, high O<sub>2</sub> deposition atmosphere of 400mTorr, and immediately cooled in the same atmosphere. Ex-situ anneals were reported as necessary for CuAlO<sub>2</sub> film growth.

Yanagi et. al. published<sup>17</sup> "Electronic structure and optoelectronic properties of transparent p-type conducting CuAlO<sub>2</sub>"(2000). This work is a follow-up publication from the same team in the first report. It offers few details on deposition parameters. The ones given were temperature of 690°C,  $O_2$  deposition pressure of 9.7mTorr, a laser fluency of 5 J cm<sup>-2</sup>, and a frequency of 20Hz. The procedure now includes a post-deposition in-situ annealing, and a much higher fluency, closer to what is found in other publications. The post-anneal time, under the same deposition atmosphere, was 3h. The  $O_2$  pressure was kept at the same pressure while cooling down to room temperature. Crystal structure analysis in this work state that "epitaxially grown films should show a higher mobility than the polycrystalline films obtained in this present study".

Neumann-Spallart et. al. published<sup>27</sup> "PLD growth of CuAlO<sub>2</sub>"(2007). This work investigates the possibilities of making the crystalline material by various annealing procedures. Target to substrate distance, fluency, oxygen pressure and substrate temperature were optimized with the aim of obtaining films of maximum specific conductivity (similar to values reported previously). All as-deposited films were X-Ray amorphous. In-situ post annealing (15min-8h) was reported to have no effect on film properties. As-deposited X-ray amorphous films on sapphire were annealed at 1050°C in air for 5 to 10 minutes. The procedure is not detailed, but it appears that a Rapid Thermal Annealing procedure was following. Annealing results in crystallization with highly preferential orientation. short annealing times were reported as helpful to suppress formation of impurities of other phases,

but that these cannot be avoided. The authors stress that they did not find crystallinity (and at the same time conductivity) in as-deposited films. The conditions reported to yield maximum conductivity are a temperature of 690°C,  $O_2$  pressure in the deposition chamber of 400mTorr, a laser fluency of 3.5 J cm<sup>-2</sup>, and a deposition frequency of 20Hz.

### CuAIO<sub>2</sub> Growth by Reactive Magnetron Sputtering followed by RTA

The following publications do not follow the same methodology as the present work, but the resulting analysis is similar enough to be of interest. The fabrication procedures for the precursors are completely different, but they have the same required compound composition.

Shy and Tseng published<sup>28</sup> "Characterization of CuAlO<sub>2</sub> thin film prepared by rapid thermal annealing of an Al<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O/sapphire structure" (2005). This publication reports that CuAlO<sub>2</sub> thin films were successfully prepared by depositing a sandwich structure (Figure 2.1) composed of Al<sub>2</sub>O<sub>3</sub>/Cu<sub>2</sub>O/sapphire, by sputtering. Then treating this sample to a rapid thermal anneal in air, above 1000°C.



 $\text{Cu}_2\text{O} + \text{Al}_2\text{O}_3 {\rightarrow} 2\text{CuAlO}_2$ 

Figure 2.1- A typical sandwich structure of Al<sub>2</sub>O<sub>3</sub> (200 nm)/Cu2O (500 nm)/sapphire before and after annealing.

The films grown were epitaxial, as measured by the Laue method and a conductivity of 0.57 S/cm was obtained for the films. The authors propose an interface between CuAlO<sub>2</sub> and Sapphire to be  $[010]_R/[1100]_H$ , quite different than the interface proposed in this present work.

Shy and Tseng again followed up with a publication<sup>29</sup> titled "A novel method for preparing CuAlO<sub>2</sub> thin films and the film properties" (2008). Being a follow-up paper, it includes more specific details about the restrictions on their method. The most important of which is that they confirm that the heating rate must be higher than 7 °C/s in order to inhibit the formation of impurities such as CuO, and CuAl<sub>2</sub>O<sub>4</sub>. They explored annealing in vacuum and annealing in O<sub>2</sub> atmosphere, which respectively resulted in lower conductivity and more impurities.

These publications are a product from an ongoing investigation which has also resulted in Cheng-Hung Shih authoring the doctoral dissertation<sup>30</sup> titled as **"Fabrication and characterization of p-type transparent conducting oxide CuAlO<sub>2</sub> thin film"(2008)** This work, besides including additional information on the film fabrication process, describe the deposition of a multi-layer precursor, alternating between  $Al_2O_3$  and  $Cu_2O$ . It also comments on the effects of the ohmic contacts before and after annealing, and some other relevant procedural specifications. There are many details in Shih's dissertation that that support or complement the analysis performed for the present work. These will be brought to attention during the analysis of results.

### 3. Phase Diagrams featuring CuAlO<sub>2</sub>

Phase Diagrams are a type of chart used to specify the conditions (temperature, pressure, etc) by which certain distinct phases of matter exist in pure or combined state, at thermal equilibrium. Particular chemical reactions, and rates of reaction are not taken into account. If more than one pure component is present, these diagrams are called Binary Phase Diagrams. When this is the case, "composition percentage" becomes a third variable that should be included in a complete diagram.

Chemical reactions involving Cu and Al in air always involve a redox reaction by  $O_2$ , therefore complete documentation on the stabilities of the resulting compounds should technically form a Tertiary Phase Diagram, with the respective composition percentages as variables.

A factor to consider with these diagrams, is that their applicability usually varies<sup>31</sup> when the materials are in bulk or in thin films. There are many examples<sup>32,33,34</sup> for other kinds of compounds, where the thin films exhibit a wide set of contrasting boundary conditions on their phase diagrams, when compared with their bulk counterparts.

Some publications that report a phase diagram, also include more detailed information on other relevant aspects such as the energies of formation, and chemical interactions at compound boundaries. These, and other reports about the compounds of interest, are included in this section in order to be referenced during the section on film growth analysis.

In chronological order, the first relevant reference is from 1932. Von Wartenberg and Reusch<sup>35</sup> presented a phase diagram for the system  $Cu_2O-Al_2O_3$ , but did not examine any other resulting compounds. They did plot a boundary for the liquidus (maximum temperature where crystals can co-exist with the melt in thermodynamic equilibrium) in the mixture. Their result is superimposed in Figure 3.1 as a dashed line.

Misra and Chaklader<sup>36</sup> reported phase transitions found in the systems CuO-Al<sub>2</sub>O<sub>3</sub> and Cu<sub>2</sub>O-Al<sub>2</sub>O<sub>3</sub> as shown in Figure 3.1.



Figure 3.1 – Phase Diagram reported for the CuO-Al<sub>2</sub>O<sub>3</sub> system<sup>36</sup>.

There are several preliminary observations to be made on this diagram. At low temperatures, no Cu<sub>2</sub>O is formed, only CuO, which does not react with Al<sub>2</sub>O<sub>3</sub>. At around 800°C, Cu(AlO<sub>2</sub>)<sub>2</sub> = CuAl<sub>2</sub>O<sub>4</sub> begins forming in this reported narrow 800-900°C gap. It is found in equilibrium with either CuO or Al<sub>2</sub>O<sub>3</sub> when the Cu or Al concentrations are stequiometrically unbalanced. CuAlO<sub>2</sub> is reported to be stable for all temperatures between 900°C and 1260°C, and also in equilibrium with CuO or Al<sub>2</sub>O<sub>3</sub> when unbalanced.

Gadalla and White<sup>37</sup> also worked on the Cu<sub>2</sub>O-CuO-Al<sub>2</sub>O<sub>3</sub> system by heating the compounds in a thermobalance, and varying the O<sub>2</sub> pressure from 0.21atm to 1atm. A problem with the resulting diagram is that it is based on extrapolation. An important detail is that CuAl<sub>2</sub>O<sub>4</sub> was present, and found to be in equilibrium, in their samples. Results for oxygen atmospheres of  $p_{O2} = 0.21$  atm and  $p_{O2} = 0.40$  atm, are presented in Figure 3.2(A) and Figure 3.3(A) respectively.

Jacob and Alcock<sup>38</sup> contributed a new phase diagram, and also deduced a useful set of equations for the standard free energies of formation of the copper aluminates. Their experimental procedure consisted of making emf measurements on solid oxide galvanic cells. They incorporated a CaO-stabilized ZrO<sub>2</sub> electrolyte to measure oxygen potential for the mixtures Cu + CuAlO<sub>2</sub> + Al<sub>2</sub>O<sub>3</sub>, CuAlO<sub>2</sub> + CuAl<sub>2</sub>O<sub>4</sub> + Al<sub>2</sub>O<sub>3</sub>, and CuO + Cu<sub>2</sub>O from 700°C to 1100°C. The various energies of formation were used to calculate 3-phase equilibria in the system Cu<sub>2</sub>O-CuO-Al<sub>2</sub>O<sub>3</sub>. The resulting phase borders under oxygen atmospheres of  $p_{O2} = 0.21$  atm and  $p_{O2} = 0.40$  atm, are presented in Figure 3.2(B) and Figure 3.3(B) respectively.



Figure 3.2 – Isobaric section of ternary system Cu<sub>2</sub>O-CuO-Al<sub>2</sub>O<sub>3</sub> at  $p_{O2} = 0.21$  atm, as presented by (A) Gadalla and White<sup>37</sup> (B) Jacob and Alcock<sup>38</sup>



Figure 3.3– Isobaric section of ternary system Cu<sub>2</sub>O-CuO-Al<sub>2</sub>O<sub>3</sub> at  $p_{O2} = 0.40$  atm, as presented by (A) Gadalla and White <sup>37</sup> (B) Jacob and Alcock <sup>38</sup>

Data in the figures is presented in the form of a quasi-binary diagram expressed in terms of  $Al_2O_3$  and both copper oxides. This can be done by considering that  $O_2$  can be dissociated from the compounds. Ignoring oxygen, there is the same amount of Cu in 1mol CuO plus  $\frac{1}{2}$  mol Cu<sub>2</sub>O, as there is Al in 1mol Al<sub>2</sub>O<sub>3</sub>. The diagram is then symmetrical in terms of the required stoichiometry in CuAlO<sub>2</sub>.

Figure 3.2, which corresponds to air, shows that both results closely resemble each other. The only minor difference is a 50°C discrepancy in the boundary temperature at which  $CuAlO_2$  begins to form, when the composition is rich in aluminum.

When this result is compared to Misra and Chaklader (Figure 3.1), the differences are beyond just a flip of the composition scale and a switch of wt% to at%. Jacob and Alcock describe a much more rich combination of possible compounds co-existing in equilibrium. The spinel  $CuAl_2O_4$  is not only present in most of the areas, it was also found to be more stable than a mixture of the component oxides at T > 612°C. A much lower temperature than the previous results (Figure 3.1). The justification for this discrepancy is cited as the "result of the slow rate of the solid-state reactions at low temperature, which interferes with the realization of equilibrium in the studies of Misra and Chaklader".

The phase diagrams presented in Figure 3.3, were calculated at a higher  $O_2$  pressure of  $p_{O2} = 0.40$  atm. the effect is that of only slightly altering the temperature boundaries. The diagram is only included to point out the satisfactory agreement between both reports, since for the moment no work has been carried out at higher  $O_2$  pressures.

Another contribution from Jacob and Alcock's work is the calculation of the Gibbs free energy of formation for the reactions involved in the system. The results are the following:

$$2Cu_2O + O_2 \to 4CuO, \Delta G^\circ = -62,354 + 44.89T(\pm 100)$$
(3.1)

$$4Cu + O_2 + 2Al_2O_3 \rightarrow 4CuAlO_2, \Delta G^\circ = -91,510 + 39.21T(\pm 300)$$
(3.2)

$$Cu_2O + Al_2O_3 \rightarrow 2CuAlO_2, \Delta G^\circ = -5,670 + 2.49T(\pm 300)$$
 (3.3)

$$4CuAlO_2 + 2Al_2O_3 + O_2 \rightarrow 4CuAl_2O_4, \Delta G^\circ = -33,400 + 20.02T(\pm 300)$$
(3.4)

$$CuO + Al_2O_3 \rightarrow CuAl_2O_4, \Delta G^\circ = 4,403 - 4.97T(\pm 350)$$
 (3.5)

The free Gibbs energy is a measure of spontaneity for processes at constant pressure and temperature. When  $\Delta G^{\circ}$  (Change in Gibbs free energy) has a negative value it means that the process is favored and spontaneous in the forward direction. A value of zero implies equilibrium and a positive direction means that the favored direction will be the opposite of what is stated. These equations will be used to justify reactions in film growth, since all of these compounds have been observed during this work.

One example for the application of these formulae on the phase diagrams, can be presented for the copper oxides. The highly negative value for reaction 3.1 can be used to justify why no  $Cu_2O$  is found at temperatures up to 1000°C in any of the phase diagrams presented. When the temperature reaches a few hundred degrees, solid state reactions advance quickly, resulting in all  $Cu_2O$  oxidizing to CuO as predicted by eq. 3.1.

## II. Methodology

#### 4. Pulsed Laser Deposition

Lasers were invented a few decades ago in 1960<sup>39</sup>. Since then, many applications have been developed using this technology. For this work, film growth was performed by Pulsed Laser Deposition (PLD). The concept is using a high power laser irradiating directly into a target material in multiple bursts. If the beam has sufficiently high energy, the area impacted undergoes laser ablation, which means that some of this material will be removed from the target and deposited elsewhere. The first documented<sup>40</sup> study of this kind was published in 1965, where Smith and Turner used a ruby laser to make several thin film depositions. Around a decade later, with the discovery<sup>41</sup> of excimer (combination of 'excited' and 'dimer') molecules, and subsequent development of excimer laser sources, a much more convenient high-power source became available for PLD. This technique, since then, has developed<sup>42,43,44,45</sup> in such a way that it is now one of the most popular choices in the thin film research fields.

#### Excimer Laser as beam source

If a laser beam is set up to incide on a surface during a relatively long period of time, this would result in the absorbed part of the energy turning mostly into dissipated heat, which would not provoke material loss. Since a very high energy is required to provoke any type of material sublimation, a continuous laser beam is not convenient for this purpose. Excimer lasers can in fact provide this very high energy needed for material loss, in pulses lasting 10ms to 30ms. Another convenient feature of excimer lasers is that the wavelengths emitted are in the ultraviolet region. This is important because the reflectivity of most materials reduces dramatically with shorter wavelengths, resulting in more energy being absorbed for every pulse.

The laser used for this work was a Lambda Physik COMPex 110, using KrF excimer. It has an emission wavelength of 248 nm, and can provide a maximum pulse rate of 100pulses per second, with each pulse having a duration of 25ns. Considering the short bursts, the intensity of this pulsed beam could reach orders of  $10^8$ W/cm<sup>2</sup>.

#### **Deposition Atmosphere**

If the resulting ablation were to occur under atmospheric pressure, the air molecules would not permit the ejected molecules from going too far from the target. Therefore, it is required that a base vacuum be provided for the procedure. Now, in vacuum, the kinetic energy of some ejected molecules is very high, which can damage the growing film. Therefore, some sort of damping mechanism must be included. This is why a controlled pressure of a relatively heavy gas needs to be established for PLD. Depending on this pressure, the velocity at which the ejected atoms impact the surface of the substrate can be controlled.

Impacts of these atoms with the ambient molecules result in a display of fluorescence that can be visually confirmed with the naked eye. The color and shape of this plasma is an indicator of the type of interactions resulting from the impact. All these factors (beam intensity, incidence angle and ambient composition/ pressure) can be controlled so that the resulting source of vaporized target atoms can be made very dense and directed toward the substrate.

It should be noted that if some of the sublimed atoms are oxygen, it may be necessary to include  $O_2$  in the deposition ambient. This way, enough of the gaseous molecules can reach the surface of the substrate. This is yet another factor that can alter the resulting chemical composition of the deposited material.

#### Laser Ablation

There is no exact model that precisely explains or predicts the physical outcome of an impact caused by a highly energetic laser beam over a surface. It has been established<sup>46</sup> that the mechanics of ablation differs widely depending on the type of surface (ionic, covalent, or metallic). Given that the physical properties of the materials in the targets are being investigated, exact mechanisms for ablation are not usually known.

If the conditions are appropriate, the amount of energy that is not reflected is converted to enough thermal energy to break any bonding within the target. This could be equivalent to dozens of eV per atom. The remaining energy should be enough to surpass the melting and ionizing points, resulting in an excited plasma over a very small volume. This inevitably leads to an expulsion of target atoms away from the surface in a highly forward directed plasma plume.

This plume is approximately symmetric with respect to the target surface, and the distribution has been mathematically described<sup>47</sup> as  $\cos^{n}(\theta)$ , where n can vary from apx. 4 to 30, and ' $\theta$ ' is measured with respect to the normal of the surface.

In order to prevent the target from being asymmetrically deprived of material, which could result in a change in plume direction, the target can be rotated slowly. This partially corrects the problem, and also improves target utilization.

Another common effect, which was a fact for every deposition in this work, is that when the target is ablated by the beam, the chemical composition is altered. This sometimes results in a more metallic composition on the very surface of the target. If this metal happens to reflect ultraviolet light, the amount of energy absorbed will be progressively less with each turn.

For some materials, as is the case with ceramic  $CuAlO_2$ , the effect of an ever decreasing intensity in the plume cannot be overcome. In order to at least prevent this effect from

altering the conditions between film productions, light sanding of the target surface should be taken as an extra step before every deposition.

#### **Nucleation and Film Growth**

Even though the substrate may have a raised temperature, the relatively hotter atoms that have been expelled from the plasma can condense on the surface of the substrate. An important fact is that condensation is not really the only mechanism present. Atoms adhere to the surface due to attractive forces with electrochemically compatible and/or similar atoms. The exact nature of the bonding depends once again on the type of material. Since atoms adhere to the surface, this process is called adsorption, and the accumulated atoms themselves may be called adatoms. These adatoms interact with the top substrate atoms, and with each other.

The substrate in most cases needs to have a higher temperature than room temperature. Otherwise, the surface may be too cold, and adatoms may not have enough kinetic energy to arrange freely to a stable equilibrium. This may result in the film being completely amorphous or highly defective, even though the stoichiometry should suggest a more stable configuration.

Once the adatoms are on the surface of a heated substrate, several things may occur. They may, and probably will nucleate with each other. The opposite may occur, called dissociation, which happens due to thermal vibration. Adatoms may diffuse around the surface until they find a stable configuration. The adatoms may even evaporate from the substrate itself.

There are several models that describe the possible growth mechanisms when substrates are being continuously bombarded with new atoms. These models can be divided as various general types: The simplest model can assume that every atomic site in the substrate is equivalent, and may hold one adatom. The atoms are adsorbed into an immobile state, which in turn can adsorb another atom. Since there is no interaction between sites, this should result in a distribution of randomly piled up stacks of adatoms, as can be seen in Figure 4.1. This is the model that roughly resembles a substrate that is too cold during the deposition.



Figure 4.1 – Simple growth model – Randomly stacked piles of adatoms over the substrate surface. Image adopted from reference<sup>48</sup>.

**Frank-van der Merwe growth model** – In this model the dominant factor is the total surface energy of the configuration, meaning that each site is not independent of their neighbor. Therefore, the most electrochemically stable stacking of adatoms is the one with least surface area. Adatoms will then arrange each other over one single mono-layer at a time. In order for this to even begin, the adatoms must have a much stronger attraction for the atoms in the surface than to each other.

**Volmer-Weber growth model** – If the adatom-adatom interactions are much stronger than the interactions with the substrate surface, this must lead to the formation of threedimensional adatom clusters. In comparison to the Frank-van der Merwe model, many layers should stack up in order to unite all the separate islands over the substrate. Only high temperature and surface energy equilibrium may be able to produce a flat surface on the resulting film.

**Stranski-Krastanov growth model** – If the adatoms, like in the Frank-van Merwe model, have a much stronger attraction towards the surface than toward each other, then the first few atomic layers of the film will also be stacked up one single layer at a time. This
model on the other hand predicts that once the atoms are stacked up to a certain point above the substrate, maybe even a single monolayer, the adatoms start to pile up and eventually start growing as separate three-dimensional islands similar to the Volmer-Weber model.



Figure 4.2 – Visual interpretation and comparison of three growth models in thin films. Image adapted from reference<sup>49</sup>.

#### PLD System Setup

Figure 4.3 presents the parts of the PLD system used in the film fabrication process.



Figure 4.3 – Diagram of the PLD System.

The vacuum chamber (Figure 4.4), made of stainless steel, is equipped with a digitally controlled gas line (GL), which was fed only with high purity  $O_2$ . This system has a built-in target holder (TH) which has 360° of angular mobility to help centralize the plume towards the substrate (SU). The substrate itself is mechanically placed using silver paste on a heater (HT) 5cm away. This heater is powered by an electrical current provided by the heater controller (HC). The temperature of the substrate is maintained fixed using a feedback mechanism provided by a thermocouple (TC) installed in the back of the heater, and a digital controller. Care was taken to consider the actual temperature at the substrate, which required a temperature calibration before the actual depositions. This was required since the temperature of the substrate is usually tens of degrees cooler than the measured temperature in the back of the heater. Since the beam has a cross section area of about  $5cm^2$  to begin with, a biconvex lens (LE) is located in the optical path to the target in order to concentrate the light onto a smaller area. The lens-to-target distance can be adjusted to control the beam fluence.



Figure 4.4 – Stainless steel vacuum chamber with peripheral equipment.

The lowest pressure that can be achieved with this setup is approximately  $10^{-7}$  Torr. The equipment used to generate the vacuum were first a primary rotary pump from Varian, model DS-102 949-9315, and the high vacuum is performed with a turbo-molecular pump from Varian, model 9699002. Pressure was monitored with a Pirani sensor for low vacuum( $10^{-4}$  Torr), and then a Bayard-Alpert sensor for pressures around  $10^{-4} - 10^{-8}$  Torr.

Once the base vacuum was reached, the desired oxygen pressure is stabilized by injecting the oxygen flow and throttling the main valve connecting to the vacuum pump. The target is then set to rotate using a stepper motor (SM). Once the laser(LA) parameters such as frequency and beam energy are set up, everything is ready to begin deposition.

The beam is reflected from a mirror (MI), focused through the silica glass AR-coated lens, and passed through a flat silica glass entry window (EW). This relatively expensive material is necessary because regular glass is relatively opaque to the ultraviolet wavelengths, which means that most of the beam energy would be absorbed. Silica glass is not entirely transparent, but the transmission coefficient at the main wavelength is enough to produce sufficient laser ablation in the target. Another important detail is that this window must be cleaned periodically, or else the transmission will become lower with each use, due to stray material deposition on the window.

The remaining energy of the beam is what impacts the rotating target, producing a bright blue plume directed toward the substrate, that can be qualitatively monitored through any of the two observation windows (OW). The laser is set to operate for as long as it is required to obtain a desired thickness.

## 5. XRD Technique

### X-Ray Production Basics

When electrons are accelerated with sufficiently high kinetic energy and bombarded into a target atom, some of the electrons from the lowest levels (K, L, M,... corresponding to the principal quantum numbers n=1,2,3,...) may be knocked out of their orbit, leaving the target atom in an excited state. Returning the atom to a normal state requires that another electron from a higher level take its place. When electrons from the lowest level (K) are removed, any upper level electrons have a defined probability of falling to this level. Each transition results in a discrete electromagnetic emission with wavelengths in the order of several (or even fractions) of Angstroms(Å=10<sup>-10</sup>m). Since every element has unique orbital configurations, bombarding different elements result in a series of sharp characteristic peaks corresponding to each transition.

Out of the possible transitions (Figure 5.1),  $K\alpha_1$  and  $K\alpha_2$  are the most likely to occur, therefore are detected as intense peaks. Since these two wavelengths are so closely spaced together, analyses were carried out using a weighted average between their intensities.  $K\beta$  emissions are rather weak in comparison, but are also detected.

When using Cu as the target, these are the measured wavelengths:

 $K\alpha_1 = 1.540562Å$   $K\alpha_2 = 1.544390Å$   $K\alpha_{(weighted average)} = 1.541838Å$  $K\beta = 1.392218Å$ 



Figure 5.1 - X-Ray emission diagram

Its important to notice that these transitions are emitted over a continuous but weak background of wavelengths due to 'bremsstrahlung' (emission due to electron deceleration). The L $\alpha$  emissions are only slightly stronger than the background noise.

Every XRD analysis in this work was carried out using essentially monochromatic X-Rays from a Cu target bombarded with a 40kV source and a 40mV measured electron current. The wavelength used was the K $\alpha$  weighted average, and the K $\beta$  and L $\alpha$  peaks were calculated based on the K $\alpha$  diffracted angles, and were purposely ignored.

## **X-Ray Diffraction Basics**

Crystals have interplanar distances (d) in the order of Angstroms, slightly longer than the monochromatic X-Ray wavelength described before. The angle of incidence of these rays can be varied to observe at which angles there is constructive interference due to an induced phase offset.



Figure 5.2 - Bragg Reflection

The geometry of X-Ray diffraction clearly shows the Bragg Law:

(5.1) 
$$n\lambda = 2d\sin\theta$$

With ' $n\lambda$ ' being a multiple of the wavelength, 'd' an interplanar distance which can be calculated with the point group symmetry and lattice constants.

To observe the described constructive interference, the sample is rotated ( $\theta$ ), while the detector is swept at twice this angle (2 $\theta$ ). This type of scan, depicted in Figure 5.3, is called a  $\theta$ -2 $\theta$  scan. Results are typically plotted as intensity (of the diffracted x-rays) vs. 2 $\theta$ .



Figure 5.3 - Geometry of a 0- 20 scan

The crystal structure of the substrate, and Cu/Al oxides are well known and have already been reported in the literature. The PDF files used to identify each compound are found in Table 5.1.

Compound	PDF	Reference
CuAlO <sub>2</sub>	35-1401	Koehler et. al. <sup>50</sup>
CuAl <sub>2</sub> O <sub>4</sub>	78-1605	Otero et. al. <sup>51</sup>
CuO	48-1548	Langford et. al. <sup>52</sup>
Cu <sub>2</sub> O	78-2076	Restori et. al. <sup>53</sup>
a-Al <sub>2</sub> O <sub>3</sub>	46-1212	Huang et. al. <sup>54</sup>

Table 5.1 – PDF files used throughout this work for XRD analysis, and their respective references.

## 6. Electrical Measurements

### Measuring Resistivity: Van der Pauw Method

A straightforward way of measuring the resistivity of a sample is to apply a current through opposite ends, then simply measure a voltage drop using two points in its linear path. Thin films on the other hand, do not have a geometry favorable for this type of simple setup. Also, by using only two contacts, this generates uncertainty in the measurements due to undetectable parasitic voltages in the cables. The widely used Van der Pauw Method was designed to reduce these types of errors, and reliably measures the resistivity of thin films by employing a series of calculations involving simpler measurements.

The Van der Pauw method requires that the thickness of the sample be known and uniform. The electrical contacts should be small and be located on the periphery of the sample. The samples do not need to be symmetrical, but the rectangular symmetry found in most samples help control errors in accuracy.

Four electrical contacts were permanently sputtered on the corners in the surface of each sample. Details of this sputtering procedure and the preceding sample preparation will be discussed in a subsequent section.

The sample's resistance is measured as depicted in Figure 6.1. For simplicity, and only for a short moment, these two configurations will be called "horizontal" and "vertical". The position of the indices used have the following configuration:  $R_{ab,cd}$ . The currents also have a similar configuration:  $\dot{i}_{ab}$ . The definition for both indices are referenced in Table 6.1.

a	Applied Current: I+
b	Applied Current I-
с	Measured Voltage: V+

Table 6.1 – Definitions for resistance measurements in the Van der Pauw method.



Figure 6.1 – Basic "Horizontal and Vertical" configurations for resistance measurements.

The value of these resistances are defined using Ohm's law(eq. 6.1 and 6.2).

(6.1) 
$$R_{mn,op} = \frac{V_p - V_o}{i_{mn}}$$

(6.2) 
$$R_{no,pm} = \frac{V_m - V_p}{i_{no}}$$

The voltage and current's measure contacts are switched and measured again in both cases as a test for measurement repeatability and to confirm the quality of the electrical contacts.

Even better accuracy was obtained by switching the polarities of the measurements for every combination previously described. This way, the offset, parasitic, and thermoelectric voltages will cancel each other out when these resistances are averaged. Note that in this switch, both polarities must be inverted, or the only thing measured will be a sign inversion.

Both configurations previously mentioned as "horizontal and vertical" are actually the averaged result of two sets of four measurements around the permutations achieved trough combining the voltage-current switching, and the current inversion switching.

(6.3) 
$$R_{mn,op} = \frac{R_{12,34} + R_{34,12} + R_{21,43} + R_{43,21}}{4}$$

(6.4) 
$$R_{no,pm} = \frac{R_{23,41} + R_{41,23} + R_{32,14} + R_{14,32}}{4}$$

It was demonstrated in the original publication by Van del Pauw<sup>55</sup> that knowing  $R_{mn,op}$ ,  $R_{no,pm}$  and the thickness (*d*) of the samples, the resistivity ( $\rho$ ) could be resolved using:

(6.5) 
$$e^{\left(-\frac{\pi d}{\rho}R_{mn,op}\right)} + e^{\left(-\frac{\pi d}{\rho}R_{no,pm}\right)} = 1$$

Rearranging terms, the resistivity can then be calculated more directly using equation 1.6:

(6.6) 
$$\rho = \frac{\pi d}{\ln 2} \frac{R_{mn,op} + R_{no,pm}}{2} f$$

Where the new factor f is related to geometrical considerations, mainly the size and shape of the contacts, substrate dimensions, and thickness uniformity in the sample. The factor has a value of f=1 when the sample has perfect symmetry, and decreases following the relation:

(6.7) 
$$\cosh\left\{\frac{R_{mn,op}/R_{no,pm}-1}{R_{mn,op}/R_{no,pm}+1}\frac{\ln 2}{f}\right\} = \frac{1}{2}e^{\ln \frac{2}{f}}$$

This factor, as can be seen from eq. 6.7, decreases with the relation  $R_{mn,op}/R_{no,pm}$ . The numerical values are illustrated in Figure 6.2.



Figure 6.2 – Graphical representation of f as a function of  $R_{mn,op}/R_{no,pm}$ 

Low values in factor f are indicative that a sample has too many geometric irregularities. The most probable source of error in most cases would be a non-uniform thickness. A value of at least 0.7 (representing an order of magnitude between the measured resistances) should be

used as criteria to determine that the sample is adequately uniform and suitable for electrical measurements<sup>56</sup>.

### **Hardware Setup**

Appropriate measurement devices need to be used to perform the Van der Pauw technique to measure resistivity and Hall Mobility. Table 6.2 specifies the instrumentation used as each measuring component. Details such as range and capabilities for each equipment are described subsequently.

Component	Instrument
D.C. Current Source	Keithley Model 2400
Picoammeter	Keithley Model 6485
Nanovoltmeter	Keithley Model 2182
Switching Mechanism	Keithley Model 7065/ Keithley Model 7001
Electromagnet	G.M.W. Model 3472-70
Magnetic field sensor	DIM-133 / MPT 230

 Table 6.2 – Components used for electronic measurements.

**D.C. Current Source (Keithley Model 2400)** – Necessary to supply the constant current specified in the techniques. This specific equipment has the capacity to supply currents from 1 $\mu$ A up to 1A. The equipment also has the direct capacity to measure two-point resistance. In this alternate configuration, it has a stand-alone range from 20 $\Omega$  up to 200M  $\Omega$ .

**Picoammeter (Keithley Model 6485)** – Monitors the current supplied by the constant source. The equipment ranges from 1pA up to 1A. The sample rate could go as high as 100 measurements per second.

**Nanovoltmeter (Keithley Model 2182)** – Low noise measurements can be obtained with this equipment, measuring resulting voltages down to the order of  $10^{-9}$ V.

**Switching Mechanism (Keithley Models 7065/7001)** – Model 7001 is a housing on which one or two expansion cards can be installed. This housing supplies the front panel for direct access to cards capabilities, and also provides the interface to control the card trough a computer link. Keithley Model 7065 is a Hall Effect Card, providing the four contacts that are to be physically connected to the sample. Internally, this card operates a series of relays to permute the electrical contacts. This reduces significantly the errors associated with disconnecting and repositioning the electrical contacts on the sample. This card has internal limits of 10V, and is capable of withstanding currents of 1A.

**Electromagnet (G.M.W. Model 3472-70)** – This electromagnet consists of two large coils wound up in the same direction, with a small and adjustable gap (82mm max.) between them(Figure 6.3). The coils can withstand a current of 70A when cooled properly with running water. If the gap is to be reduced to a mere 0.5mm, 3.5T can be achieved. Considering the dimensions of the sample holder, magnetic fields of around 0.9T can be achieved. The equipment receives current from a power supply model 63C 60110 Power Ten, and is complemented with a current reversal equipment G.M.W model 5970-80.



Figure 6.3 - G.M.W.® Electromagnet Model 3472-70

**Magnetic Field Sensor (DIM-133 / MPT 230)** – The equipment labeled as model MPT 230 is the sensor itself, named a "Miniature High Sensitivity Hall Probe". It measures fields up to 3T, with a resolution of  $50\mu$ T and precision within 0.03%. The equipment labeled as model DIM-133 is the system containing the microprocessor that encodes the magnetic field and relays the result to the computer link.

The sample holder is a sapphire wafer with four thin, but rigid, metal contacts that are encrusted into the wafer, resulting in all four of them protruding in both sides. The contacts that go to the measuring equipment can be soldered on one side, and the sample can be soldered on the other. The sample is held mechanically with a small amount of thermal paste. A small length high gauge Au wire was soldered with indium, both on the contacts of the sample, and the contacts on the "sample side" of the holder.

Independently shielded copper wires were soldered with indium to the other side of the wafer. The copper wire eventually connects to BNC type connectors and sends the voltages/currents trough four shielded coaxial cables straight to the measuring equipment.

### Software Setup

All of the mentioned equipment can be connected trough a PCI-GPIB 488-21 data bus. Therefore by the nature of this link, every equipment can be monitored and controlled using a separate computer.

The programming language used for control of this system was based on LabView 7.0. All of these components have a separate, but customizable driver, designed for Labview. The merging combination of all these control algorithms result in a system that is composed of easily manageable virtual panels. This system has been set up mostly recently as a separate work<sup>56</sup>. With few modifications, it has been proven to systematically perform all of the resistivity and Hall effect measurements within desired accuracy. An outline sketching the process can be seen in Figure 6.4.



Figure 6.4 – Outline sketching the measuring process. The subpicture of the equipment depicts the Keithley devices with model number 2400(DC Supply), 2182 (Nanovoltmeter), 7065/7001(Hall effect card holder) and the 6485(Picoammeter) Left to right, and top to bottom respectively.

## **Contact preparation procedure**

Four ohmic contacts on the sample are required to make the electrical measurements. These were fabricated using a DC Sputtering technique with appropriate sequential masking.

After samples were annealed, found phase pure by XRD analysis, and the thickness were measured by profilometry, samples were treated by sand etching.

Samples are masked using the cloverleaf geometry (depicted in Figure 6.5), which is suggested by Van der Pauw<sup>55</sup> to favor symmetry and reduce measurement errors. Sand etching, performed on the exposed areas of the sample, is a process that consists of injecting a stream of air with copious amounts of finely powdered alumina directly into the target region. After a few minutes of etching, the resulting geometry on the sample is clearly visible with the naked eye. The resulting central region of the film is only about three millimeters wide.



Figure 6.5 – Cloverleaf geometry suggested for Hall coefficient measurements.

Samples were then partially covered with two strips of oil-free aluminum foil to serve as a mask during the sputtering process. Both strips were carefully cut to a size just under the dimensions of the borders of the remaining sample, as can be seen in Figure 6.6.



Figure 6.6 – Masking the samples. (Not drawn to scale).

The remaining flaps on the foils are bent over the back of the substrate, resulting in a small package with only four small corners of the film exposed. These corners are prepared to be fractions of a millimeter wide. This is necessary due to the conditions specified by the Van der Pauw method.

The exposed areas for the contacts were then coated with a standard DC Sputtering procedure. The masked samples were introduced in singles or in batches into a vacuum chamber, where a base pressure of at least  $5 \times 10^{-5}$  Torr was achieved. An Argon atmosphere was introduced with a controlled pressure of 12 mTorr. Sputtering targets need to be cleaned of all oxides and impurities found on their surface, so pre-sputtering into a removable shield was necessary before making any contact deposition.

Contacts were prepared using either Au or Al. The only problem is that neither of them adheres very well to the surface of the film. On the other hand, Cr does adhere to both films and Au/Al, but making contacts out of pure Cr results in much lower conductivity. Therefore, deposition was divided in two parts to maximize adherence and conductivity. It is possible to make the depositions one after the other without breaking vacuum because the system is set up to have two separate sputtering guns and the sample holder can be rotated into either one of them.

Samples were placed 7cm away from the targets. After the target surface cleaning procedure, which was powered at 15W during 3 minutes, a first layer of Cr was deposited onto the sample at 50W during 8 minutes. Immediately afterwards, the Au (or Al) target was also cleaned and deposited using the same durations.

## 7. Target Preparation

Two successful procedures for fabricating CuAlO<sub>2</sub> targets used for laser ablation will be detailed. Both finalized targets were found by XRD Analysis to be of sufficiently high purity CuAlO<sub>2</sub>. While the first procedure proved successful enough, the second was found to be of even higher purity, and was the one used for laser ablation.

### Procedure #1: Corundum(Al<sub>2</sub>O<sub>3</sub>) and Tenorite(CuO)

A mixture of both chemicals in powder form was used as precursor to sinter  $CuAlO_2$  as specified in the following reaction after heating:

$$2CuO + Al_2O_3 \rightarrow 2CuAlO_2 + \frac{1}{2}O_2$$

With a final goal of sintering a 1" diameter x 1/4" maximum thickness pellet, assuming the bulk density of 5.1g/cm3, a total mass of 16.4123g would be required before heating. Considering a mass reduction ratio of 8/124 due to oxygen loss in the reaction, a mass of 15.3512g should be expected.

In order to keep careful stoichiometry, a balance with a resolution of  $1 \times 10^{-4}$  grams (Model: Denver Instruments XE-100.) to weigh the following mass:

74/124 CuO = 9.7935g – (purity of 98%, grain size < 5um, from Aldrich Co.) 50/124 Al<sub>2</sub>O<sub>3</sub> = 6.6175g – (purity of 99.8%, grain size < 10um, from Aldrich Co.)

CuO was first ground by hand using an Agate mortar in order to reduce any relatively large grains of the material. The same procedure was not repeated with Al<sub>2</sub>O<sub>3</sub>, since it is such a hard compound to break physically by this procedure.

Once the mixture was appropriately weighed, it was mixed mechanically for 1h, in 15 min. intervals using the ball mill grinder depicted in Figure 7.1.



Figure 7.1- Mechanical Grounding/Pre-Mixing Equipment

This mixture was then finely ground using a Micronising Mill with Agate pellets (Model: McCRONE, Figure 7.1), while mixed with isopropyl alcohol(propanol), for 1 hour, in 15 minute intervals.



Figure 7.2 – Agate Pellets with Micronising Mill

The propanol solvent was evaporated from the mixture using a high power halogen lamp, as shown in Figure 7.3.



Figure 7.3 – Solvent Evaporation

Only a portion of this powder was used when pressing the 1" diameter pellet. The remaining material was stored as backup, and later also used as part of the annealing procedure.

The powder that was used for the pellet, was compacted using a hydraulic press. 10Klbs of force, equivalent to a pressure of approximately 900N/cm<sup>2</sup> were applied to the sample during 30 minutes. After compacting the powders, the resulting precursor pellet resulted with a measured mass of 12.2187g.

This pellet was then heated to 1,100°C with a furnace (Lindberg Blue M, model BFS1333C) The heating ramp used was +5°C/min, the pellet was kept at 1,100°C for a period of 24h, then cooled down at a slower rate of -2°C/min.

After this first heating, the pellet effectively reduced in mass to 11.4670g. This value is within 0.3% of the expected mass reduction due to oxygen. The volume of the pellet increased considerably, but the composition, as revealed by XRD Analysis (Figure 7.4), resulted in mostly CuAlO<sub>2</sub> peaks with only a few impurities.



Figure 7.4 – XRD Analysis, CuAlO<sub>2</sub> pellet ( from CuO+Al<sub>2</sub>O<sub>3</sub> - first heating)

The resulting pellet was again ground by hand with the agate mortar, and the entire procedure was repeated. Micronization, evaporation of the solvent, pressing and reheating were repeated with the same conditions, but his time using a heating ramp of  $+10^{\circ}$ C/min, sintered at 1,100°C for a period of 24h, then cooled down at a rate of  $-2^{\circ}$ C/min.

The volume of this re-heated sample did not measurably increase, suggesting that the observed volume increase from the first heating was due to oxygen from the reaction trapped within the target.

The XRD Analysis, shown in Figure 7.5, from this second heating shows that most of the impurities have disappeared from the pellet, resulting in a sufficiently pure target that could be used for laser ablation.



Figure 7.5 – XRD Analysis, CuAlO<sub>2</sub> pellet (from CuO+Al<sub>2</sub>O<sub>3</sub> - second heating)

Even though this target can be effectively used, the second procedure that follows seems to produce a better result.

# Procedure #2: Corundum(Al<sub>2</sub>O<sub>3</sub>) and Cuprite(Cu<sub>2</sub>O)

The second procedure, the one that was finally used for the ablation procedure is essentially the same, but it employs another phase of copper oxide. The chemical reaction during sintering is the following:

$$Cu_2O + Al_2O_3 \rightarrow 2CuAlO_2$$

According to the reaction, the correct stoichiometry to produce a 1" dia. by 3/16" CuAlO<sub>2</sub> pellet, is:

 $66/116 \text{ Cu}_2 \text{O} = 9.3360 \text{g} - (97\% \text{ Purity, grain size} < 5 \text{um, from Aldrich Co.})$  $50/116 \text{ Al}_2 \text{O}_3 = 7.0740 \text{g} - (99.8\% \text{ Purity, grain size} < 10 \text{um, from Aldrich Co.})$ 

This mixture is prepared using the same conditions and equipment as before, but since it is not solid enough when pressed, and reduces to powder when handled, it was found that fabrication of the pellet requires 5-7% stearic acid. This additional component is used as a binder for the mixture. The compound remains solid at atmospheric pressure, but liquefies at the higher pressures used during the procedure. This additional step ensures that when the precursor powders are pressed together, the stearic acid liquefies and saturates the pellet. When the pressure is removed, the acid returns to solid state, effectively binding both powders together. This compound conveniently evaporates during the heating process.

When compacting the mixture, only 9Klbs of force were required, equivalent to a pressure of approximately 800N/cm<sup>2</sup>. A relatively smaller pressure is required, since the stearic acid also seems to bind the powders to the borders of the compacting cylinders.

This pellet was then heated using a ramp of +10°C/min, sintered at 1,100°C over a period of 10h, then cooled down at -2°C/min. The XRD Analysis shows in Figure 7.6, that even with the first heating, this procedure already shows higher purity.



Figure 7.6 – XRD Analysis, CuAlO<sub>2</sub> pellet ( from Cu<sub>2</sub>O+Al<sub>2</sub>O<sub>3</sub> - first heating)

This pellet was again ground by hand with the agate mortar, and the whole procedure was repeated as well with the same conditions.

The heating ramp was raised once again to  $+40^{\circ}$ C/min, sintered at 1,100°C during a period of 10h, and then cooled down at a rate of  $-2^{\circ}$ C/min.

The XRD Analysis, shown in Figure 7.7, effectively shows the purity of the sintered CuAlO<sub>2</sub> target.



Figure 7.7 – XRD Analysis, CuAlO<sub>2</sub> Pellet ( from Cu<sub>2</sub>O+Al<sub>2</sub>O<sub>3</sub> - second heating)

## 8. Sample Annealing Procedures

Annealing is defined as a heat treatment for samples after they have been deposited. There are many ways to alter these heat treatments. The main factors to consider, besides temperature, are the heating/cooling rates, and the duration of the heat treatment. There are also other important aspects to consider, such as atmosphere during the process, and the immediate vicinity around the sample.

#### In-situ Annealing

The term "in-situ", adopted from Latin, literally means "in the place". In the context of thin film fabrication, it means the annealing took place in the same site where the sample was deposited.

In this case, in-situ annealing can be performed easily. After the deposition, the temperature of the heater on which the sample is placed, can be directly controlled. The oxygen pressure is also a factor that is easy to maintain. Every control mechanism is already integrated and no additional handling of the sample is necessary. On the other hand, possible heating and cooling rates are limited, and very fast rates in particular are not possible.

### **Ex-situ Annealing**

Under similar context, "ex-situ" annealing means that the sample is heat treated in an external furnace or heating equipment. This additional processing of the sample is necessary when the annealing requirements are beyond the limits of the heater used in the deposition chamber.

Since the annealing temperatures required for  $CuAlO_2$  fabrication are several hundreds of degrees over the safe limits of the deposition heater, two external furnaces were used to heat treat the samples prepared in the work.

The first is a Lindberg Blue M, model BFS1333C, which is capable of holding a sustained temperature of 1500°C, and has a programmable 16 step heat ramp control. The inconvenience with this furnace is that the insulation required to maintain these temperatures result in a relatively high thermal mass. This in turn has the effect of considerably slowing down the maximum possible heat and cool rates. Working at full power, the furnace requires 3h to reach 1,050°C, and around 18h to cool down to room temperature.

The second furnace used in this work was a Thermolyne Type F47918. This equipment has a small (Width: 12.7 cm. Height: 10.2 cm. Depth: 15.2 cm.), and vented heating chamber. These reduced dimensions, and smaller capacity heating elements, limit its continuous use to 1093°C, but the furnace is capable of holding intermittent (3h max.) temperatures of up to 1200°C. The smaller thermal mass of this furnace therefore requires 1h to reach 1,050°C, and around 9h to cool down to room temperature. Figure 8.1 plots the more precisely measured maximum cooling rate for this furnace.



Figure 8.1 – Cooling rate for furnace after heating elements are turned off.

#### **Rapid Thermal Annealing – Preliminary Justification**

CuAlO<sub>2</sub> is only one of the possible compounds resulting from the multi-variable ternary system: Cu<sub>2</sub>O-CuO-Al<sub>2</sub>O<sub>3</sub>. The phase diagrams,<sup>37,36,38,57</sup> show that given certain conditions such as composition, temperature, and oxygen pressure, the resulting compounds on the film could be either CuO, Cu<sub>2</sub>O, Al<sub>2</sub>O<sub>3</sub>, CuAlO<sub>2</sub>, CuAl<sub>2</sub>O<sub>4</sub>, or a combination of these. Obtaining phase purity for the copper-aluminates (CuAlO<sub>2</sub> and CuAl<sub>2</sub>O<sub>4</sub>) is not a simple task. As can be seen from the phase diagrams presented, combinations of phases are the most stable long-term configurations at most temperatures.

An effective way to isolate and control phase composition, is to use the fact that phases have different stabilities at different temperatures and atmospheres. If the film temperatures are rapidly altered before the film has had enough time to reach thermal equilibrium, it is possible to have a measure of control, and favor growth of a specific phase.

The heating and cooling rates of conventional ex-situ furnaces, even in the relatively small models as shown in Figure 1.1, are not fast enough to isolate and grow specific phases. Therefore, since faster cooling rates are necessary, a furnace needs to be adapted for a rapid thermal process.

### **Rapid Thermal Annealing – System Setup**

The same model F47918, described previously, has an air vent on the top. This aperture, 2.8cm in diameter, was originally designed by the manufacturer to prevent the heat generated inside from altering the pressure on the chamber, and therefore unwillingly altering the annealing atmosphere for a given process.



Figure 8.2 – Furnace Model F47918. Arrow indicates air vent.

This vertical duct, was adapted to work as a channel to access a midpoint around the interior of the chamber and introduce and retrieve samples at a controlled speed so that much faster temperature ramps could be obtained than allowed by the furnace itself. Two heating elements are located on opposite walls of the furnace, with a regulating thermocouple located near the center of the chamber. This configuration guarantees that when a sample is inserted linearly, the temperature can be maintained constant when held near the relatively wide center(~3cm) of the chamber.

The sample holder, depicted in Figure 8.3, which was to be inserted trough this aperture, was fabricated from a sheet of stainless steel bent in the shape of an open box. A stainless steel wire is incorporated in a way such that it holds the bottom face of the structure. The resulting holder can be described as a steel basket with a volume of approximately 1cm<sup>3</sup>.



Figure 8.3 – Fabricated Sample Holder from two view points.

The sample holder then has to be introduced mechanically down to a mid point in the chamber as a reproducible process. The setup for this procedure consists of the sample holder in a mechanical arrangement, so that it can be displaced vertically by a stepper motor as shown in Figure 8.4.



Figure 8.4 – Diagram representing the motor/sample holder configuration.

The motor is driven by a microprocessor controller (system pictured in Figure 8.6), which can be configured to trigger a certain number of steps, and adjust the time intervals between each step, thereby controlling the heating and cooling rates separately.

The sample is lowered from a point outside the furnace from a point sufficiently high to be considered room temperature, down to a mid-point inside the furnace where the temperature has been regulated. A diagram illustrating and scaling the system is shown in Figure 8.5.



Figure 8.5 – Diagram illustrating the scale of the system, and resolution of the stepper motor.



Figure 8.6 – Pictures illustrating the RTA setup.

The stainless steel in the holder will undoubtedly suffer debilitating corrosion from oxidation at temperatures as high as 1,200°C. The change in temperature also has the effect of tempering the steel, making it harder and thus more fragile with each rapid cooling. Eventually, the walls of the holder become so thin and rigid, that they crumble with handling, and a new one must be fabricated. It is a nuisance with the process which must be repeated around every dozen anneals.

It has been reported<sup>14</sup> that to avoid substantial material loss, the anneals should be carried out with the samples face down over mixed powders of CuO and Al<sub>2</sub>O<sub>3</sub>. This practice did seem to work on long ex-situ anneals. Therefore, it is reasonable to keep this as part of the process, even if rapid thermal anneals take only minutes. Another publication<sup>27</sup> advises that the film should not be covered, since a release of oxygen is hindered from the reaction:

$$CuO + CuAl_2O_4$$
.  $\rightarrow 2CuAlO_2 + \frac{1}{2}O_2$ 

In practice, this reaction can also proceed the other way around. Considering the Gibbs free energy associated with the reaction, eq. 3.4 indicates that it will in fact proceed in reversal if there is additional  $Al_2O_3$  present in the sample.

To avoid contamination of the sample, and to avoid risking surface imperfections, the sample was kept from direct physical contact with these powders by resting in ceramic separators. However the samples resulted with inconsistencies in color where there was contact with the separators. Better results were obtained by placing the samples face up.

The holder system has a relatively small mass in total, and since it was fabricated with stainless steel, it also has a low specific heat capacity. These factors contribute to the fact that the furnace temperature controller can quickly adjust for the additional inserted thermal load. As soon as the holder is introduced in the furnace, the controller immediately regulates back to the previously sustained temperature set point.

#### **Rapid Thermal Annealing – System Characterization**

The temperature dependence in the path of the holder is clearly non-linear, with an abrupt rise in temperature when entering the chamber. The curve describing the measured temperature as a function of distance from the furnace center is shown in Figure 8.7. Measurements were made in each point when an inserted thermocouple reached thermal equilibrium.



Figure 8.7 – Abrupt rise in temperature as measured trough the linear path of the sample holder. The furnace was kept at the controlled temperature of 1150°C.

When the linear rate of motion of the sample holder is changed in the microcontroller setup, the speed of translation of the sample can be controlled directly. While the temperature variation with displacement is non-linear, it can in principle be linearized with careful calibration and programming of the microprocessor. In practice, however, this non-linearity in the path can be considered transient if the rate of motion is fast enough. Since sample mass was very small in all cases, there is little thermal inertia and sample temperature can be equalized to the ambient rapidly.

In the microprocessor setup, the delay between each step can be as high as desired, and as low as 3ms/step. Given the number of steps in the path, and an addition of a constant 1.4ms/step for internal instructions, the fastest time interval capable for the linear path is only 10s. The temperature measured by an inserted thermocouple, on the other hand, takes 30s to

reach equilibrium. Therefore, 30s to reach thermal equilibrium at the highest temperature can safely be considered a lower limit for the system when raising the temperature at the fastest rate.

Figure 8.8 depicts the fastest heating rate capable by the system. Figure 8.9 shows how by raising the delay between each step, the heating rate is proportionately reduced.



Figure 8.8 – Temperature rise in the process as measured by a thermocouple on the sample holder. The heating step rate for this case is 3ms/step.



Figure 8.9 – Temperature rise as measured when the heating step rate is slowed down to 200ms/step.



Figure 8.10 - Temperature drop as measured when the cooling step rate is 3 ms/step.

The temperature drop rate is now clearly exponential. A visual confirmation that the sample holder is the main factor, and not the thermocouple, is that the sample itself takes approximately 20s to reach the Draper point (temperature of approximately 525°C, where all objects stop glowing dimly red due to thermal radiation.)
# III. Results and Discussion

# 9. Crystal structure orientation for CuAlO<sub>2</sub> in Sapphire

#### Substrate Structure Analysis

The substrate used to grow the films was **c-cut sapphire** (oriented and polished corundum, or  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>, cut along the basal plane of the hexagonal unit cell.) Sapphire has a rhombohedral primitive cell with space group symmetry R<sub>3</sub>c (group #167). The lattice of this primitive unit cell is more easily visualized when converted into the hexagonal non-primitive unit cell. The resulting basal plane after the hexagonal conversion is depicted in Figure 9.1.

The rhombohedral-to-hexagonal conversion for the R3c group leads to stricter reflection conditions. The most important of which, considering that the substrate is cut along the basal plane (00l) is that l = 6n, where n is an integer. This means that the only reflection planes allowed are (006), (0012), (0018) etc. Every other plane is prohibited due to additional internal atoms in every conventional unit cell. This is easily visualized with the six layers of Oxygen atoms along the c direction in the conventional unit cell depicted in Figure 9.2.



Figure 9.1 – *Left Image* - (0001) plane for  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> or "c-cut sapphire". The other lattice constant (not depicted for clarity) is c=12.9929Å directed toward ±z

Figure 9.2 – *Right Image* - *a*-Al<sub>2</sub>O<sub>3</sub> Hexagonal unit cell. Filled circles represent Al atoms, and open circles represent O atoms.

However, several samples have exhibited the forbidden plane reflections of (003) and (009), at around  $2\theta$ =20.5° and  $2\theta$ =64.5° respectively. The unexpected nature of these peaks is confirmed if Bragg's law is applied to the corresponding multiple of the interplanar distance. What triggers these peaks is still unknown, since some samples may actually gain or lose the "forbidden peaks" before or after annealing. The present speculation is that they appear due to unintentional doping of the substrates, deformation twin planes, or some other sort of deformation along the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> crystal structure. Either way, considering that the peaks were experimentally confirmed to be only part of the imperfect substrate, they can be safely ignored from the  $\theta$ -2 $\theta$  scans.

### CuAlO<sub>2</sub> Plane Structure Analysis

Delafossite structures, including CuAlO<sub>2</sub>, are referenced to have a rhombohedral primitive cell with a space group symmetry of:  $R\overline{3}m$  (group #166). This crystal structure, depicted in Figure 9.3, can be treated as having a hexagonal unit cell with three lattice points in each unit volume.



Lattice constants for the hexagonal unit cell configuration in CuAlO<sub>2</sub>:

a= 2.858Å c= 16.958Å

Figure 9.3 – Hexagonal unit cell for CuAlO<sub>2</sub> (Image adapted from publication<sup>58</sup>). The layers marked as (\*) are called the edge sharing layers, and the layer marked (†) will be used in a future reference.

The rhombohedral to hexagonal conversion for this space group now places restrictions on the reflection conditions (n being an integer)<sup>59</sup>:

(h00): h=3n, (0k0): k=3n, (hkl): l=3n, (hk0): h-k=3n, (h0l): h-l=3n, (0kl): k+l=3n, (00l): l=3n

In general, the rhombohedral configuration will always follow this rule: (hkl): -h+k+l=3n when transformed into the hexagonal configuration<sup>59</sup>.



Figure 9.4 – One particular case of unit cell conversion. Depicted in (A) are rhombohedral  $(001)_R$ planes, now equivalent to (B) hexagonal  $(0\overline{1}11)_H$  planes.

Knowing the conversion formulas, we find that the most important restriction for this work lies on the family of basal planes (00l), where l = 3n, n being an integer.

### Preferential Growth for CuAlO<sub>2</sub> // (c-cut Sapphire)

Due in part to the similarity between structures, phase pure films over c-cut sapphire exhibit clear and exclusive preference for the (003), (006), (009), (0012) family of basal planes.



Figure 9.5 – CuAlO<sub>2</sub> phase pure sample. Peaks marked \*Kα and \*Kβ are due to the (006) plane of the sapphire substrate, diffracting from the main and secondary wavelength emissions for Cu.

Since it has already been established that rhombohedral structures will appear as (*ool*): l = 3n when indexed as structurally hexagonal, this is a clear indication that CuAlO<sub>2</sub> thin films are strictly oriented along the c-plane of sapphire.

# 10. Precursor Depositions

CuAlO<sub>2</sub> thin film fabrication procedure by PLD is divided in two steps. Precursor deposition, and sample annealing, both of which are crucial for single phase crystal formation, and will be discussed in two separate chapters.

#### As-Deposited Phase Purity by PLD

There have been only two publications, by Kawazoe et. al.<sup>26</sup> (1997) and Yanagi et. al.<sup>17</sup> (2000) who, using the same equipment, have reported single phase polycrystalline  $CuAlO_2$  to grow as-deposited by PLD. No other reports have been found with reproductions of these results. What has been observed in other works, including this present investigation, is partial growth of CuAlO<sub>2</sub>, but never in pure phase form, and too insulating to yield reliable electrical measurements. As Stauber-Perkins et al.<sup>14</sup> stated in their publication: "...using very similar deposition parameters, such findings were not substantiated. Target properties may have a certain influence there....". Even though target crystal structure is not generally considered a crucial factor in laser ablation, this statement is plausible. There have been some publications that show how sintering conditions for the material can significantly alter the structure of the material in bulk<sup>60</sup>. This same publication cites that "thermoelectric properties of CuAlO<sub>2</sub> ceramics were significantly dependent on sintering temperature". Target density is another factor that affects laser ablation mechanisms. This property, and surface morphology, as shown by SEM imaging<sup>61</sup>, are also dependent on temperature soak times. Variables during the target sintering process were not investigated, but may be an area of interest for future work.

As-deposited phase-pure  $CuAlO_2$  films have not been reliably established as a viable option. The question then arises as to what is an appropriate deposition procedure that can be considered a convenient precursor for subsequent anneals.

### Precursor Types – Resulting Compounds

The deposition parameter ranges that were investigated in this work can be divided according to results, into three different broad categories of reproducible precursors.

- X-ray-Amorphous Precursor.
- Partial CuAlO<sub>2</sub> Precursor.
- *Cuprite (Cu<sub>2</sub>O) Precursor.*

These categories are not named because the x-ray analysis of the as-deposited films exhibit the mentioned compound exclusively. They are just the defining characteristic found in the as-deposited films. Al<sub>2</sub>O<sub>3</sub> peaks may be present in the XRD analysis, and CuAl<sub>2</sub>O<sub>4</sub> peaks can also be present in the film. The only two preferred orientations of CuAl<sub>2</sub>O<sub>4</sub> observed are (111) at  $2\theta$ =19.011°, and (511) at  $2\theta$ =59.397°. The fact that these two orientations are by far not the most intense peaks when compared to the PDF<sup>51</sup>, can only mean that CuAl<sub>2</sub>O<sub>4</sub> is also favored to grow oriented with respect to c-cut sapphire (used as a substrate for all samples). Details on this orientation are not important, since the CuAl<sub>2</sub>O<sub>4</sub> phase is undesirable for this investigation.

#### X-ray-Amorphous Precursor

This type of precursor appears to be the one featured in the other two reports<sup>14,27</sup> on CuAlO<sub>2</sub> growth by PLD. Their only characteristic, as seen from XRD analysis, is a lack of any discernible compound peaks. This does not necessarily imply that the deposited material is truly amorphous. A possible interpretation is that a crystal structure is present, but the lattice is so defective that there is no detectable long-range order from the diffracted x-rays.

The PLD parameter that favors this type of precursor is low deposition temperature. The range goes from room temperature, up to 650°C. A typical XRD result is shown in Figure 10.1.



Figure 10.1 – Sample deposited at room temperature. Peaks marked as \* are from the sapphire substrate.

Depositions at room temperature result in the samples having macroscopic irregularities after they are annealed, even when observed under an optical microscope with a low amplification of x100. This might serve as an additional indication that the sample has a highly defective structure which is worse as deposition temperature is lower. Since no XRD peaks were observed from the films, it was not possible to evaluate its composition. However, from the nature of the PLD procedure, it is expected that film composition for the metals is nearly the same as for the target.

These precursors are not entirely unsuccessful after being annealed. The resulting films are mostly  $CuAlO_2$ , but as a side effect, every anneal performed on these types of precursors, results in apparently inevitable  $CuAl_2O_4$  impurities, as shown in Figure 10.2.



Figure 10.2 – Annealed film resulting from an amorphous precursor. (T<sub>anneal</sub>=1,050°C, and an anneal time of 2 minutes by RTA)

The publications on the material synthesized by PLD and annealed afterwards, agree that these impurities could not be eliminated. The films measure strong  $CuAlO_2$  peaks, but with the same  $CuAl_2O_4$  impurities. According to this present work, the possible explanation is that both previous studies were carried out using amorphous precursors. Their reported XRD results can be found in Figure 10.3.



Figure 10.3 – Published works featuring samples with annealed amorphous precursors: Stauber et. al<sup>14</sup> (top), Neumann et. al.<sup>27</sup>(bottom). Peaks marked as § are from CuAl<sub>2</sub>O<sub>4.</sub>

As was found for all other depositions, if there is any amount of  $CuAl_2O_4$  present in the precursor, none of the ranges of anneal ramps tested helped to remove this impurity. The stubborn phase will remain in the film regardless of the annealing temperature, up to at least 1150°C, which referring to the phase diagrams in Figure 3.2, is bordering on the highest temperature phase boundary where  $CuAlO_2$  is stable. None of the equations stating the Gibbs free energies of formation (3.1 - 3.5) shows a tendency to favor a reaction from  $CuAl_2O_4$  to  $CuAlO_2$ . Equations 3.4 and 3.5 on the other hand, establish  $CuAl_2O_4$  as the most stable of all the oxides in the ternary system.

A relatively high  $O_2$  deposition pressure(100 - 400mTorr), as seen in the previous two publications<sup>14,27</sup>, is at least one of the factors contributing to CuAl<sub>2</sub>O<sub>4</sub> formation in the precursors. It is not clear why this is observed, but when the oxygen pressure is dropped to 10mTorr, CuAl<sub>2</sub>O<sub>4</sub> is no longer found in the as-deposited films.

### Partial CuAlO<sub>2</sub> Precursors

The laser deposition parameters described by Yanagi et. al.<sup>17</sup> are more specific than the conditions described by Kawazoe et. al.<sup>26</sup> but both report the same results. Their values, reported to yield pure phase CuAlO<sub>2</sub> films are:

- Substrate Temperature of 690°C
- $O_2$  Pressure in deposition chamber of 1.3Pa = 9.7mTorr
- Energy density at target of 5 J/cm<sup>2</sup>/pulse
- Laser repetition frequency of 20Hz
- The sample was then annealed in-situ for 3h at the same deposition atmosphere.

These deposition conditions were repeated for the present work, and strong CuAlO<sub>2</sub> reflections were indeed observed, but it was not found to be phase-pure. XRD Analysis of the sample shows at least three other oxides: CuAl<sub>2</sub>O<sub>4</sub>, Cu<sub>2</sub>O, and Al<sub>2</sub>O<sub>3</sub>. Results are plotted in Figure 10.4.



Figure 10.4 – Results obtained by using the same conditions reported by Yanagi et. al.<sup>17</sup>

As was discussed in the previous section, the presence of  $CuAl_2O_4$  in the resulting film makes this an inconvenient precursor, since subsequent anneals will not be able to remove this particular impurity.

### Cuprite (Cu<sub>2</sub>O) Precursor

This type of precursor can be defined as having Copper (I) Oxide as the only Cu compound observable in XRD Analysis. There seems to be no preferred orientation on the sapphire c-plane surface, since at least one of these three orientations are observed in the resulting precursor:

- (110) at 2θ=29.583°
- (111) at  $2\theta = 36.442^{\circ}$
- (200) at 2θ=42.329°

Some samples have also resulted in one wide (018) peak of  $Al_2O_3$  at 20=61.298°.

No differences were observed in the resulting annealed films if there are different orientations present for  $Cu_2O$ , or if the  $Al_2O_3$  peak is present. Figure 10.5 to 10.7 represent the types of XRD patters that fall in this category of precursors. All peaks marked with an asterisk(\*), are reflections from the sapphire substrate.



Figure 10.5 – Cuprite precursor with observed peaks of (110), (111), (200), and Al<sub>2</sub>O<sub>3</sub> in (018).



Figure 10.6 - Cuprite precursor with observed peaks of (110), (111), and Al<sub>2</sub>O<sub>3</sub> in (018).



Figure 10.7 - Cuprite precursor with observed peaks of (111), (200), and no peaks of Al<sub>2</sub>O<sub>3</sub>

This type of precursor has been the only one observed in this investigation to yield phasepure and conducting CuAlO<sub>2</sub> samples. The PLD conditions to obtain these precursors are near the ones reported by Yanagi et. al.<sup>17</sup>, but the in-situ anneal was not employed in the present conditions. As soon as the deposition was finished, the current to the heater and the oxygen atmosphere were abruptly shut off, therefore the films were cooled down to room temperature while the atmosphere remained in vacuum.

- Substrate Temperature of T = 700 °C during deposition.
- O<sub>2</sub> Pressure in deposition chamber of 10mTorr.
- Energy density at target of 4 J/cm<sup>2</sup>/pulse. (With an energy beam of 95mJ)
- Laser repetition frequency of 10Hz.

The  $O_2$  pressure during deposition seems to be a trade-off. If there are less oxygen molecules in the atmosphere, it is reported that there is a higher preference for Cu<sub>2</sub>O over the other copper oxides<sup>62</sup>. On the other hand, lower  $O_2$  pressure is also reported to produce lower conductance in the samples<sup>27</sup>.

The deposition parameters for this type of precursor should definitely be more systematically studied and fine tuned, since deposition temperature for Cu<sub>2</sub>O growth by PLD can shift the film's preferred orientation from (200) to  $(111)^{62}$ . Exploring if these orientations improve conductivity or crystallinity in the subsequently annealed films could also be considered as a future research possibility.

### **Deposition on Glass Substrates**

Deposition of  $CuAlO_2$  over a glass substrate is not a promising idea for at least two reasons. First, the amorphous nature of glass by definition lacks a crystal structure over which the material can grow epitaxially, or at least in a favored direction. The low melting point of glass substrates is also a problem, because it cannot be heated to temperatures above the glass softening point. For SiO<sub>2</sub> glass, although higher than for ordinary glass, this limit is approximately 800-900°C, which is too far below the temperatures required for CuAlO<sub>2</sub> phase stability. Disregarding these drawbacks, a deposition using the same target was made over a glass substrate using similar parameters. Results for the XRD scan are shown in Figure 10.8.



Figure 10.8 – As deposited film on a SiO<sub>2</sub> substrate.

Results only reveal reflections for polycrystalline CuAl<sub>2</sub>O<sub>4</sub>, compensating with CuO to meet the 1:1 ratio of Cu:Al. No traces of CuAlO<sub>2</sub> or even Cu<sub>2</sub>O are present in the sample. Further annealings, raised as high as 900°C were attempted. Results, plotted in Figure 10.9, show that the sample is essentially left unchanged at these temperature ranges. The broad peak by  $2\theta \approx 21^\circ$  is due to the amorphous nature of glass. Any amorphous material from the film itself is indistinguishable from the substrate.



Figure 10.9 – Subsequent annealings of a sample deposited on SiO<sub>2</sub>.

# 11. Annealing the Samples

There are few parameters left to consider when annealing the precursors. They are now reduced to: anneal temperature, heating/cooling rates, anneal time, and atmosphere. The finer details on the process were discussed in Chapter 4. For convenience with the nomenclature, plain "ex-situ" will be applied for samples annealed with the furnaces where the conventional method was used. Rapid Thermal Anneals, performed with the adapted equipment, although also considered "ex-situ", will be referred only as "RTA". Since "in-situ" anneals were discarded as part of the precursor process, the atmosphere was not a parameter that could be varied. Given the present equipment, all anneals were performed in air.

### Establishing the Annealing Temperature

Of all the possible ranges reported in the phase diagram for  $CuAlO_2$ , when the compound is in equilibrium, it is always coexisting with another Al or Cu oxide. If thin films with a composition ratio of 1:1 for Al:Cu are exposed to temperatures higher than T = 1000°C, the time required for the compounds to reach equilibrium is in the order ranging from fractions of an hour, to several hours as the temperature is lowered.

Sample annealing in longer times (3h) can induce substantial material loss by evaporation, which can be seen by inspection or by XRD analysis, as illustrated in Figure 11.1.



Figure 11.1 – Sample annealed at 1,200°C for 3h. Visual inspection seems to corroborate substantial sample evaporation.

The idea is to investigate at which temperature CuAlO<sub>2</sub> is most stable when compared to the other oxides when the sample is in the process of approaching equilibrium. A possible basis for establishing the upper time limit of 1.5h in the process of long-term reactions, is that the samples are thin films, and this is also the maximum ex-situ annealing time cited in the previous works. The temperatures tested, as suggested by phase diagrams, were in the range of 1000-1200°C. All samples used were deposited under the same conditions, and "ex-situ" annealed. The precursor type, as defined in chapter 10, was "cuprite" with small traces of CuAl<sub>2</sub>O<sub>4</sub>. This impurity in the precursors is not reason enough to discard them for the test, since the composition ratio for Cu:Al will still be 1:1, and this is the only variable that has an effect on long term equilibrium at a given temperature.

The cooling rate will undoubtedly affect the resulting composition, but since the same furnace was used (Thermolyne model F47918 - the smaller of the two available), the time elapsed when cooling from  $1150^{\circ}$ C to  $1000^{\circ}$ C is only about 5 minutes. The effect that the rest of the 9h cooling curve will have on the resulting film will be shared by all samples. The furnace might need only 2h to drop below 400°C, but the rest of the ramp keeps decreasing exponentially down to actual room temperature (~30°C).

The heating ramps for the higher temperatures are in fact longer, but it is assumed that the sample eventually reaches the target temperature where it is finally held for enough time to reach equilibrium. This assumption was later analyzed to be wrong, but the results on this test, displayed in Figure 11.2, are still useful.



Figure 11.2 – XRD results for the ex-situ annealing experiments performed at temperatures ranging from 1000 to 1200°C.

A time of 1.5h is too long for anneal temperatures of 1200°C. Samples suffer substantial material loss and the resulting films are left too thin for reliable XRD analysis. The curve illustrated for this temperature in

Figure 11.2 was carried out by rapidly heating the sample at the fastest rate possible and holding the temperature for only 15min. The sample was then cooled down to room temperature at the same rate. Even with this brief exposure, the sample already shows signs of serious evaporation. The resulting XRD peaks from the film have very low intensity, but enough information can be interpreted from the curve for it to become part of the test sequence.

These results are in excellent agreement with the updated phase diagram (for  $O_2$  pressure in air) presented by Jacob and Alcock<sup>38</sup>, already presented in Figure 3.2b. This figure is again illustrated in Figure 11.3, now with the region tested for compound stability highlighted over the image. This region is precisely the line that sweeps temperature ranges of 1000-1200°C over the path that corresponds to a molar composition ratio of 1:1 for Cu and Al.

Samples deposited at 1000°C exhibit only traces of  $CuAl_2O_4$  and CuO, just as expected from the diagram. When the temperature is raised to 1050°C, 1100°C, and 1150°C, again as expected, both  $CuAlO_2$  and  $CuAl_2O_4$  reflections are observed.

The problem that was mentioned before, of samples evaporating at 1200°C, is not found surprising when noticing that the results provided by Jacob and Alcock<sup>38</sup> place an uncertain phase boundary implying disintegration of the material around 60°C degrees away from this temperature.



Figure 11.3 – Phase diagram for  $p_{O2} = 0.21$  atm (air) presented by Jacob and Alcock<sup>38</sup>, with a featured highlight over the region tested for compound equilibrium by ex-situ anneals.

According to experimental XRD results from the test, the resulting experimental line appears to be shifted at least slightly to the right of the phase boundary corresponding to the 50% molar ratio of Cu:Al. XRD analysis show copper oxides, but no aluminum oxides. The target, prepared with enough precision, should not deviate considerably from perfect stoichiometry, but the apparently substantial and consistent shift towards higher Cu composition might most likely arise due to the very high melting point of corundum(over 2040°C), which makes it harder for the material to nucleate properly on the relatively cold surface of 700°C. Also, from the XRD results, no Al<sub>2</sub>O<sub>3</sub> reflections which were not already present due to the substrate were observed, so any Al<sub>2</sub>O<sub>3</sub> deposited is most likely amorphous.

On closer inspection over the range where  $CuAlO_2$  is stable, which was the original intention of the temperature sweep, the compositions determined by XRD analysis corroborate tendencies in phase growth suggested by the phase diagram of Jacob and Alcock. It might be noted, that the traces of CuAlO<sub>2</sub> found in the sample annealed at 1150°C are relatively stronger than the traces of CuAl<sub>2</sub>O<sub>4</sub>. Therefore 1150°C might seem like a better choice for the desired phase stability. In reality, this temperature is not practical. Instead of focusing on the relative intensities, the relevant result is that the peaks are only traces of the compounds. When the annealed films are observed trough optical microscopy, hexagonal platelets of CuAlO<sub>2</sub> are clearly visible, but with large voids around them. These voids only increase with time while the platelets themselves are diminished from evaporation. These macroscopic gaps in the film, and the anisotropy created by the large cavities and hexagonal platelets are precisely the opposite of what is required for making accurate electrical measurements on the sample. Therefore, an anneal temperature of 1150°C is also discarded from the alternatives.

The anneal temperature of  $1000^{\circ}$ C can also be quickly discarded due to a lack of CuAlO<sub>2</sub> formation. Rapid thermal anneals performed at the same temperature exhibit the same behavior: no trace of CuAlO<sub>2</sub> were observed, only CuO, and/or CuAl<sub>2</sub>O<sub>4</sub> formed.

It can also be tentatively concluded that a temperature of  $1100^{\circ}$ C clearly favors CuAl<sub>2</sub>O<sub>4</sub> growth. However, additional considerations on this result will be discussed later. Results from this test then tend to indicate that the ideal temperature for desired optimum phase stability in equilibrium conditions is around 1050°C. Similar or analogous analyses were probably carried out for previous works where ex-situ anneals were employed, since all reported studies coincide with using 1050°C as the optimal annealing temperature.

Results for this equilibrium test have been conclusive for establishing the annealing temperature, but now the effects of the duration of the anneal, and also the effects of the heating and cooling rates must be explored more carefully.

The priority is now reduced to discovering and impeding the conditions that favor  $CuAl_2O_4$  formation during the whole heat treatment. The tests described in the following section systematically altered the curves in the annealing process. The results were then analyzed, and procedures that alter the resulting phase proportions were designed.

#### Effects from the Annealing Duration

The parameter that can be controlled more easily, and is undoubtedly a crucial factor in pure phase film growth is simply the duration of the anneal. Using the same furnace, with again the same type of precursor employed in the previous test for equilibrium, the temperature was kept at 1050°C, but the anneal time was extended to double the exposure (3h). The test also measures longer-range equilibrium at the given temperature. Results are presented in Figure 11.4. The key observation in this comparison is the proportion of the relative intensities between phases in both samples. The sample annealed for 3h clearly shows how the CuAl<sub>2</sub>O<sub>4</sub> has increased in proportion to CuAlO<sub>2</sub>. Therefore, longer annealing times are counterproductive.



Figure 11.4 – Comparison of two samples annealed for 1.5h, and 3h, at 1050°C.

When the anneal time is lowered much further, by treating the samples (with the RTA system) to anneals down to 40 seconds, the tendency is clear. Shorter annealing times help suppress  $CuAl_2O_4$  in favor of  $CuAlO_2$ , but generates CuO, another type of impurity. Similar impurities have been reported by the other publications on  $CuAlO_2$  growth by PLD that employ subsequent anneals<sup>14,27</sup>.

An important conclusion from this investigation is that the CuO impurities are not really a problem. A very short dwell time turns out to be the most crucial factor when preparing CuAlO<sub>2</sub>. Details on this final parameter will be discussed by the end of the analysis.

#### Effects from the Annealing Ramp Rates

The first preliminary test in order to study the effect of these parameters is basically extending both ramp lengths. This was done crudely by performing the same original 1.5h anneal at 1050°C, but with the Blue M furnace model BFS1333C, which has a much higher thermal inertia. Results are presented in Figure 11.5.



Figure 11.5 – Comparison of samples annealed for 1.5h at 1050°C, but using two furnaces with different thermal masses, resulting in extended heating and cooling ramps for the heavier of the set.

The comparison clearly shows that slower ramp rates favor  $CuAl_2O_4$  completely over  $CuAlO_2$ . At this stage, it can be concluded that at least one of the ramps must proceed at a faster rate than provided by the natural cooling curve of the relatively faster furnace.

A simple method was used to determine whether phase pure CuAl<sub>2</sub>O<sub>4</sub> is formed during the heating or the cooling ramp. A sample was introduced in the heavier of the furnaces, using

the same sequence where pure  $CuAl_2O_4$  is expected, but after approximately 10 minutes at the highest temperature, the door of the furnace chamber was abruptly opened, and the sample quickly removed from the furnace using long pliers. The procedure is potentially dangerous if not performed with extreme caution, but the method is a sort of rudimentary "Rapid Thermal Cooling". The XRD result from a sample after undergoing this procedure is illustrated in Figure 11.6.



Figure 11.6 – XRD Result from rapidly cooling a sample by removing it from the furnace while operating at the highest temperature set-point of 1050°C.

Interpreting this result is straightforward. If the rate is slow,  $CuAl_2O_4$  is unquestionably formed while heating the sample. If the heating rate is even slower, phase pure oriented  $CuAl_2O_4$  will be easily obtained.

It has been already discussed that  $CuAlO_2$  is not produced from  $CuAl_2O_4$ . It is then not surprising that even though  $CuAlO_2$  might also be stable in the ranges 1050-1150°C, when the sample reaches these target temperatures, there will be no other oxides left in the precursor other than  $CuAl_2O_4$ . The film will remain phase pure for all remaining annealing times. This actually explains why in the original temperature sweep, samples annealed at 1100°C exhibit no  $CuAlO_2$  peaks at all. By the time the furnace reaches that temperature, all traces of  $CuAlO_2$  have already been converted into  $CuAl_2O_4$ . For now, the only reason remaining as to why  $1100^{\circ}$ C is not a convenient anneal temperature, is because higher temperatures accelerate chemical reactions. This is not necessarily desirable when fabricating CuAlO<sub>2</sub>, since there is always the threat of obtaining CuAl<sub>2</sub>O<sub>4</sub>. One more reason against annealing at 1100°C will be explained later.

Up to now,  $1050^{\circ}$ C has been the optimal anneal temperature, and it has been clearly established that short anneal times, and faster heating rates are indispensable requirements for hindering CuAl<sub>2</sub>O<sub>4</sub> growth. The next natural step in this investigation is to explore what is the optimal heating rate which least favors CuAl<sub>2</sub>O<sub>4</sub>.

Using the RTA setup described in Chapter 8, much faster heating rates were tried. In summary, the rates of 3ms/step, 12ms/step and 30ms/step are roughly equivalent to having the sample reach 1050°C in approximately: 36°C/s, 24°C/s, and 12°C/s respectively. A more accurate curve for this heating rate is found in Figure 8.8. The samples were annealed for 2 minutes, and the cooling rate for all cases was consistently kept at the fastest value. This experiment was not officially designed with the presented structure, so it must be mentioned that due to procedural circumstances, the sample heated at the rate of 12°C/s was performed at 1,100°C. It might not fit exactly in the sequence, but serves as an indicator of the tendencies mentioned in this text. Results for this experiment can be found in Figure 11.7.



Figure 11.7 – Resulting XRD for samples heated at increasing rates.

Rate of 12ms/step shows a very slight trace of  $CuAl_2O_4$ , with orientation (511) located at  $2\theta$ =59.397°. The trace is not very clear in the picture, so the plot is again repeated and amplified in Figure 11.8. It is important to mention that his almost negligible trace was already present in the precursor. The reason why it was not discarded, and used for this test, was to verify that a rate of 12ms/step, and an anneal duration of 2min at 1050°C are fast enough to limit CuAl\_2O\_4 growth, even if it is already present in the sample.



Figure 11.8 – Amplification of the curve depicted as "12ms/step" in Figure 11.7.

The important conclusion that can be derived from this test is to show that if rate proceeds even faster(at most 24°C /s), and the dwell temperature is not above 1050°C,  $CuAl_2O_4$  growth is effectively halted.

On the other hand, faster heating rates with lower annealing dwelling times, or higher temperatures, have the tendency to produce CuO impurities. This is a relevant topic deserving some additional attention.

### Remarks on the formation of CuAlO<sub>2</sub> from CuO and Al<sub>2</sub>O<sub>3</sub>

The overall reaction to produce CuAlO<sub>2</sub> from CuO and Al<sub>2</sub>O<sub>3</sub>, presented by Neumann-Spallart<sup>27</sup>, at least for fabricating targets, is:

$$2CuO + Al_2O_3 \rightarrow 2CuAlO_2 + \frac{1}{2}O_2$$

This reaction was not included in the set of Gibbs equations presented by Jacob and  $Alcock^{38}$ , so no preference can be attributed with respect to eq. 3.5:

$$CuO + Al_2O_3 \rightarrow CuAl_2O_4$$

As was hinted before, CuO impurities by themselves are not a serious problem. In fact, if a sample only has shown  $CuAlO_2$  and CuO phases, it might even be re-annealed as many times as necessary, and the impurities will seem to disappear. An example of this procedure is presented in Figure 11.9.



Figure 11.9 – Subsequent re-anneals, 2minutes each, at temperatures of 1050°C for the first one, and 1100°C for the others.

Apparently it is possible to obtain pure phase  $CuAlO_2$  from subsequent anneals, but this alternative has not been fully explored. One detail that must be mentioned which influences the lack of attention towards this prospect is that for some reason that same sample was measured to be highly insulating after annealing. A reasonable explanation might be that

traces of CuAl<sub>2</sub>O<sub>4</sub> are still present in the sample when these are annealed over multiple instances.

Another detail that was not mentioned in the precursor analysis, is that although small CuO impurities may be removed from CuAlO<sub>2</sub>, if CuO is found as-deposited, equation 3.5 will proceed to CuAl<sub>2</sub>O<sub>4</sub>, since it can readily react with available alumina(Al<sub>2</sub>O<sub>3</sub>).

This is why the more favorable precursors have Cu in the form of Cu<sub>2</sub>O. If Cu<sub>2</sub>O reacts with  $O_2$ , it reduces to CuO. If the annealings are carried out in air, it might seem like this is inevitable, but what could be happening is the model described by Shy et al<sup>28</sup>. Since the heat ramp rate is fast enough, Cu<sub>2</sub>O melts before it completely oxidizes to CuO. This melted oxide then reacts with alumina in a peritectic reaction, forming solid CuAlO<sub>2</sub> according to reaction 3.3. The process is depicted in Figure 11.10.



Figure 11.10 – Schematic for CuAlO<sub>2</sub> growth. Model suggested by Gonzalez et. al.<sup>57</sup> Picture adapted from publication<sup>30</sup>.

There is then one last reason to consider the anneal temperature of  $1100^{\circ}$ C as inconvenient. According to eq. 3.1, Cu<sub>2</sub>O reacts with O<sub>2</sub> easily, to form CuO. If the sample temperature is raised. This reaction will proceed more quickly, in turn resulting in possible production of CuAl<sub>2</sub>O<sub>4</sub>.

If the samples are annealed from precursors which contain only  $Cu_2O$ , a possible alternative for the observed appearance of crystallized CuO in the resulting samples is that liquid  $Cu_2O$ did not have enough time to react with alumina completely, and simply oxidized during cooling, which proceeds at a slower rate. Then, if CuO is observed in the resulting anneal, it appears to be an indicator of insufficient dwelling time at the annealing temperature.

### Final deposition duration and conditions.

The parameters have now been established for determining the limiting range at which  $CuAlO_2$  is meta-stable, and phase pure.

- The precursor must only include Cu<sub>2</sub>O and Al<sub>2</sub>O<sub>3.</sub>
- The heat ramp must be as fast as possible. (the system limit of 36°C/s was used in this work).
- Dwell time must be long enough to react all of the melted Cu<sub>2</sub>O, but not as long as to permit formation of CuAl<sub>2</sub>O<sub>4</sub>. from CuAlO<sub>2</sub>.

Finding the optimal growth condition is now just a matter of sweeping different time intervals for the anneal duration.

As can be seen from Figure 11.11, a relatively short anneal duration of approximately 2.5 minutes, combined with the previously discussed conditions, resulted as the optimal single-phase  $CuAlO_2$  thin films.



Figure 11.11 –Samples annealed at 1050°C, and at different anneal dwell times.

### Remarks on plausible explanation for CuAl<sub>2</sub>O<sub>4</sub> persistence.

An explanation for this persistent  $CuAl_2O_4$  phase might be that the substrate is slowly providing Al atoms and shifting the Al:Cu composition to the left part of the phase diagram (Figure 11.3). Noting that the substrate is in fact a large reservoir of  $Al_2O_3$ , it should not be surprising that at elevated temperatures, it can react with the film and produce  $CuAl_2O_4$ . This may be why films always have such a strong tendency towards the Al rich copper oxide  $CuAl_2O_4$  under almost every parameter, specially elapsed time. If the process indeed occurs, the concentration of  $CuAl_2O_4$  would be higher towards the substrate. Unfortunately for the present work we did not have access to analytical techniques which can probe composition as a function of depth, and this must remain for future work about this problem.

### 12. Electrical Measurements

A few pure phase samples were tested for electrical conductivity. The sample that exhibited the best conductance and overall quality was measured, and the results are displayed with more detail in the following section.

#### **Resistivity Measurements**

The factor (*f*) that serves as a test for sample uniformity were determined for this sample. A value of f = 1 indicates perfect symmetry. Since the system incorporates an additional cyclic test for the contacts, a total of two factors ( $f_A$ ,  $f_B$ ) were generated for the confidence test. The dimensionless results are as follows:

 $f_A = 0.9946$  $f_B = 0.9945$ 

The values are near unity, which is a clear indication of uniformity, and are very similar to each other, which is an additional indicator that the sample is geometrically symmetric. The two values for the calculated resistivity, as follows from equation 4.7, are as follows:

 $\rho_{\rm A} = 0.5880 \ \Omega \cdot m$  $\rho_{\rm B} = 0.5865 \ \Omega \cdot m$ 

Again, the similarity between the values is not surprising given the overall symmetry of the sample. With an error percentage of only 0.25%, the average, which is the actual functional result, is  $\rho = 0.58726 \ \Omega \cdot m$ .

The conductivity of the highest conducting sample of the present study is then:

#### $\sigma$ = 0.0170 S/cm

When compared to previously reported values, it is still about an order of magnitude below those included in Table 2.1, but these values specify only the highest conductivity using the aforementioned methods. If this conductivity is compared to most of the other works, this value can be considered relatively high.

### **Hall Effect Measurements**

Hall effect measurements could not be obtained using the method previously described. The samples were too resistive for the present equipment. An alternative measuring method must be employed for future work on this material.

# 13. Φ Scan Technique: Confirming epitaxial growth

Epitaxial growth can be loosely described as crystals growing aligned in two dimensions. It has already been discussed that the crystals are growing perpendicular to the c-plane surface, but in order to establish epitaxial growth, there must be evidence that the crystals are also oriented with respect to the hexagonal surface itself, not just the plane.

In order to measure if there is any fixed angular position between the single sapphire crystal and the film,  $\Phi$  orientations for both must be measured independently, and then compared to see if thy hold any type of correlation between the angles.



Figure 13.1 - **Φ** orientation of the substrate.

Regular  $\theta$ -2 $\theta$  scans of materials that are completely c-plane oriented, like the substrate, will never detect any new peaks around  $\Phi$  rotations because planes that depend on this angle (for example, the family of planes: 024,  $\overline{2}04$ ,  $2\overline{2}4$ )(Figure 13.2) will effectively rotate with  $\Phi$ , but will always diffract at a given angle ( $\chi$ ) away from the direction of the detector(Figure 13.3).



Figure 13.2 - α-Al<sub>2</sub>O<sub>3</sub> oriented corundum, (sapphire) planes

Given the  $R\overline{3}c$  space group symmetry, there will be three sets of planes that diffract around one full  $\Phi$  rotation. Using the geometry of the plane inside the hexagonal cell, we can calculate the angle ( $\chi$ ), between the (024) plane and the (001) plane, and tilt the sample in that same direction(Figure 13.4).



Figure 13.3 – Standard 0-20 scan aligned around multiples of the (001) plane (c-cut)



Figure 13.4 – Substrate tilted at an angle of  $\chi$  in order to align the (024) family of planes

Since the new planes are now oriented in the direction where the c-planes should have been, when the sample is rotated around ( $\Phi$ ), a sharp peak should be observed for every rotational symmetry around this angle. Given of course that ( $\theta$ ) be remained fixed at an angle calculated using Bragg's Law using the new interplanar distances.

For this work, the  $\Phi$ -dependent plane selected was  $(024) = (02\overline{2}4)_H$  due to its relative intensity and reasonable ( $\theta$ ,  $\chi$ ) inclination.



Angles for the  $\Phi$  scan around the (024) family of planes in sapphire:

### Φ Scan: Experimental results for Sapphire

The highly pure phase and strongly oriented sample that resulted in Figure 9.5 was selected to perform the  $\Phi$ -scan. Using the specified angles for sapphire as parameters, the scan, plotted in Figure 13.5, resulted as expected:



Figure 13.5 – Substrate  $\Phi$ -scan
The peaks have an intensity several orders of magnitude over the background noise, leaving no doubt over the exact angular position of the (024) family of planes. The positions of the peaks themselves serve as reference points as to where the planes are located with respect to the sample. The most important characteristic observed in this result is that there are only three peaks measured, and that they are equidistant around one full rotation. This effectively proves that the substrate is a single crystal, with the expected symmetry for the space group.

## Φ Scan: Experimental results for the CuAlO<sub>2</sub> film

Now the whole process has to be repeated but recalculating the angles for CuAlO<sub>2</sub>. The same criteria were used for selecting  $(018) = (01\overline{18})_H$  as the family of planes, both for their relative intensity, and for their reasonable  $(\theta, \chi)$  inclination.

$2\theta = 2 \cdot \sin^{-1} \left( \frac{\lambda}{2d} \right) = 57.16^{\circ}$	
$\chi = \tan^{-1}$	$\left(\frac{\begin{array}{c}c_{CuAlO_2}\\l\\a_{CuAlO_2}\\k\end{array}\right) = 40.58^{\circ}$

Angles for the  $\Phi$  scan around the (018) family of planes in CuAlO<sub>2</sub>:

If the film were actually a single crystal, the space group symmetry of  $R\overline{3}m$  should make the scan result similar to sapphire: three sharp equidistant peaks.

If the film were not epitaxial, there should be no peaks at all for this  $\Phi$ -scan, implying that the film is not oriented "in plane". The obtained result definitely strikes out this possibility, since sharp peaks were observed in the film itself.



Figure 13.6 – CuAlO<sub>2</sub>  $\Phi$ -scan. Dashed lines represent the angular positions of the (024) family of planes measured from the sapphire substrate(Figure 13.5).

This proves that the film grows epitaxially. An important observation is that there are six peaks instead of the three expected. This could only mean that the crystals have two possible growth orientations. The other important fact is that both sets of three peaks are shifted  $30^{\circ}$  from the sapphire substrate orientation, and both sets (which represent the two possible growth directions) are shifted  $30^{\circ}+30^{\circ}=60^{\circ}$  from each other.

## 14. Geometry of the CuAlO<sub>2</sub> // Sapphire interface

Now that both lattice constants are known, and that the  $CuAlO_2$  orientation is known with respect to the substrate, the interface between them can be deduced from the geometry of their chemical bonds.

The lattice constants (Figure 14.1) have a direct lattice mismatch of approximately 40%; therefore, a direct stacking configuration is not reasonable.



Figure  $14.1 - (001) = (0001)_{\text{H}}$  orientations for both sapphire and CuAlO<sub>2</sub> drawn to a relative scale with their respective lattice constants.

Therefore we must take a step by step approach to understanding the alleged growth structure. This mechanism was modeled to be analogous to one described<sup>6</sup> for the growth of CuGaO, another delafossite which by the way also serves as an alternative for fabricating a p-type transparent conducting oxide.

First we begin with the basal plane surface of the substrate (001), and consider that as can be seen in the unit cell in Figure 9.2, every Al atom at the surface will bond with three close pack shaped oxygen atoms.



Figure 14.2 – Substrate surface terminated in oxygen.

Since the  $CuAlO_2$  unit cell also contains a layer of hexagonally close packed oxygen atoms (marked as (\*) in Figure 9.3), these turn out to align quite well in the lattice, and can therefore serve as the oxidized layer in the substrate(Figure 14.3).



Figure 14.3 - Hexagonal close packed layer in CuAlO<sub>2</sub> aligned with the surface of the sapphire substrate.

It must be noticed that the lattice constants in these drawings are rendered at a relative atomic scale. With this in mind, we can visually confirm a lattice mismatch that should result in some internal strain. Following simple geometrical calculations around the lattice constants, the lattice mismatch is found to be **3.86%**. From the diagram, we can also observe why there was a 30° shift between the crystal structures.

To explain why there are two sets of crystal orientations for the material shifted 60° from each other, one must again consider the symmetry of the hexagonal unit cell. If we only notice the layer marked as (†) in Figure 9.3, we can see how this space symmetry should result in two possible growth orientations (Figure 14.4).



Figure 14.4 - Diagram representing the two possible crystal orientations.

Given that there is no preference for either, both cases are equally likely to occur. This could be evidenced by the intensities measured in Figure 13.6 not having any remarkable differences.

## **IV.** Conclusion

A new approach on  $CuAlO_2$  thin film sample fabrication was developed, and has been proven to be a viable alternative to fabricate conducting samples. The approach consists of depositing "Cuprite" type precursors which are composed of  $Cu_2O$  and  $Al_2O_3$  by PLD, followed by a short RTA dwell time. Epitaxial growth on c-cut sapphire has been established for the films, and a model for the interfacing structure with c-cut sapphire has been included in the analysis.

The available literature on  $CuAlO_2$  thin film growth was unclear and conflicting, but this work clarified crucial aspects on  $CuAlO_2$  thin film fabrication. The investigation detailed in this publication helps solve some of the ambiguities found in the literature in relation to compound stabilities.

The highest measured conductivity of  $0.017 \text{ S} \cdot \text{cm}^{-1}$  is still about one order of magnitude lower than optimized results from previous reports, but this work presented an original approach to CuAlO<sub>2</sub> thin film production on which to build future investigations. The range of research possibilities is still very wide, and it should still be possible to improve the electrical characteristics of the material substantially. Some suggestions for improving and following up on this work are presented in the following section.

#### **Future works**

Some of these research possibilities definitely would interact with each other and indeed this should be encouraged, since these are the conditions that must be optimized in order to improve on the conductivity of the samples.

• Exploring non-stoichiometric ratios in the target preparation.

A possible explanation for the success in finding phase purity, is because some of the Al atoms found in the substrate, thus shifting the composition towards the Cu rich region of the phase diagram(Figure 11.3), where CuAlO<sub>2</sub> is stable. If a target were to be prepared which was purposely deficient in Al atoms, the precision required in the anneal times might not be as critical. This might even be the reason why the work carried out by Hernandez <sup>63</sup> favors CuAlO<sub>2</sub> growth with a higher concentration of Fe dopants, which are introduced by reducing the Al:Cu ratio in the PLD target.

#### • Optimizing RTA time-scales by altering the anneal temperature.

The ubiquitous anneal temperature of  $1050^{\circ}$ C should actually be fine-tunable. The basis for this statement is the broad behavior observed in the compound stabilities for the temperature ranges of  $1000-1200^{\circ}$ C (Figure 11.3). Apparently, the rates of formation for CuAlO<sub>2</sub>, and CuAl<sub>2</sub>O<sub>4</sub> are significantly dependent over this temperature range. Total anneal times should also be significantly dependent on the anneal temperature. This might help reduce the margin of error that would arise from anneals that require specific times ranging in the order of seconds.

#### • <u>Optimizing O<sub>2</sub> deposition atmosphere for the precursors.</u>

Since conductivity has been reported to be dependent on oxygen pressure during precursor deposition, this is a possibility that should not be ignored.

### • Exploring annealing procedures under different deposition atmospheres.

The same procedure explored in this work might be used as basis to find the new temperature ranges to make experiments measuring compound equilibrium under a higher oxygen pressure, as can be seen in the modified phase diagram depicted in figure 3.3b. This would be under the same assumption that oxygen pressure affects sample conductivity.

## • Exploring slower cooling rates.

Shy et. al.<sup>29</sup> have reported that the cooling ramp is a critical parameter that must be tweaked in order to observe higher conductivity in the samples. This possibility was not tested in the present work, but is certainly not discarded as a serious option to optimize the electrical characteristics of the samples.

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