FORMATION OF $CuAlO_2$ THIN FILMS BY ULTRASONIC SPRAY PYROLYSIS FOR PHOTODIODE APPLICATIONS

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FORMATION OF $CUAlO_2$ THIN FILMS BY ULTRASONIC SPRAY PYROLYSIS FOR PHOTODIODE APPLICATIONS

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Iping Suhariadi

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LIST OF ABREVIATION

AFM	:	Atomic Force microscopy
CSD	:	Chemical Solution Deposition
CVD	:	Chemical Vapour Deposition
EDS	:	Energy dispersive spectroscopy
EHD	:	Electrohydronamic
FESEM	:	Field emission scanning electron microscopy
ITO	:	Indium Tin Oxide
ICDD	:	International Conference for Diffraction Data
SPA	:	Semiconductor parameter analyser
LED	:	Light Emitting Diode
PL	:	Photoluminescence
TCO	:	Transparent Conducting Oxide
TG/DTA		Thermogravimetric/Differential Thermal Analyzer
USP	:	Ultrasonic Spray Pyrolysis
UV-Vis	:	Ultraviolet-Visible
VBM	:	Valence Band Maximum

LIST OF SYMBOLS

A	:	Surface Area (cm^2)
$\%A$	:	Absorption
F_g	:	Gravitation Force ($Kgms^{-2}$)
F_e	:	Electrical Force (Coulomb)
F_s	:	Stokes Force (N)
h	:	Planck constant (eV.s)
I	:	Current (A)
I	:	Intensity (Lux)
G	:	Free Gibs Energy
l	:	Length (m)
N	:	Number of Particles
μ	:	Mobility ($cm^2V^{-1}s^{-1}$)
R	:	Resistance (Ω)
$\%R$	:	Reflectance
S	:	Enthalpy (Joule)
T	:	Temperature (°C)
t	:	Thickness (cm)
ρ	:	Resistivity (Ωm)
σ	:	Conductivity (Sm^{-1})
υ	:	Frequency (Hz)

LIST OF PUBLICATIONS

1. Iping Suhariadi, Zainovia Lockman, Sabar D Hutagalung, Kamsul Abraha, Atsunori Matsuda. (2010) The formation of $CuAlO_2$ thin films by nitrate route chemical solution deposition method. Proceeding. The 3rd Regional Conference Interdisciplinary on Natural Resources and Material Engineering. October 2010. Malaysia

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PEMBENTUKAN FILEM NIPIS $CuAlO_2$ MELALUI TEKNIK

PIROLISIS SEMBURAN UNTUK APLIKASI FOTODIOD

ABSTRAK

$CuAlO_2$ merupakan oksida jenis –p yang lutsinar. Apabila digabungkan dengan bahan jenis n, simpang p-n akan terbentuk dan boleh digunakan di dalam pelbagai aplikasi menarik optik dan elektronik. $CuAlO_2$ filem yang sekata, bebas daripada retakan dan homogen telah dihasilkan melalui proses pemendapan cecair kimia melalui teknik pirolisis semburan ultrasonik di atas substrat silicon jenis n yang telah dibersihkan. Prapenanda cecair yang digunakan adalah campuran $Cu(NO_3)_23H_2O$ dan $Al(NO_3)_39H_2O$. Parameter pemendapan yang mempengaruhi sifat-sifat filem adalah kadar aliran gas pembawa, jarak muncung-substrat, suhu substrat dan nisbah Cu kepada Al telah dikaji. Parameter yang optimum telah diperolehi untuk pemendapan filem: kadar aliran gas, 1 L/min, jarak muncung-substrate, 3 cm, suhu substrat 550 °C dan nisbah Cu kepada Al adalah 1.2:1. Aliran titisan daripada kebuk melalui muncung adalah laminar pada jarak dan kadar aliran gas pembawa ini. Pembentukan filem dicadangkan melalui tindakbalas pirolitik antara ion-ion Cu dan ion-ion Al di dalam setiap titisan apabila menghentam substrat yang panas. Imej SEM untuk sample yang optima memnunjukkan filem terhasil mempunyai butiran dengan ketebalan ~1.9 µm. Spektroskop UV-Vis telah menunjukkan filem terhasil mempunyai jurang tenaga 3.54eV dan kelutsinaran melebihi 60 % dalam julat cahaya nampak. Kekonduksian filem adalah 0.354 Scm^{-1}. Filem menujukkan sifat diod apabila simpang-p $CuAlO_2$/-n Si dihasilkan dengan aliran voltan sekitar 0.4 V. Di bawah iluminasi cahaya nampak yang berlainan kuasa, diod menujukkan sifat-sifat kesan fotoelektrik.

FORMATION OF $CuAlO_2$ THIN FILMS BY ULTRASONIC SPRAY PYROLYSIS FOR PHOTODIODE APPLICATIONS

ABSTRACT

$CuAlO_2$ is a p-type oxide which is transparent. When coupled with an n-type material, a p-n junction can be created and can be used in many interesting optical and electronic applications. Smooth, crack free and homogenous $CuAlO_2$ film was produced by chemical solution deposition process via ultrasonic spray pyrolysis (USP) technique on a cleaned n-type Si substrate. The precursor solution used was comprised of a mixture of $Cu(NO_3)_2.3H_2O$ and $Al(NO_3)_3.9H_2O$. The deposition parameter influences the film properties are the flow rate of carrier gas, nozzle-substrate distance, substrate's temperature and Cu to Al ratio was studied thoroughly. The optimum parameters were found for the films deposited at a flow rate of 1 L/min, nozzle-substrate distance of 3 cm, substrate's temperature of 550°C and Cu to Al ratio of 1.2:1. The flow was seen to be laminar at this distance and flow rate of carrier gas. The formation of films was proposed to be due to the pyrolytic reaction of Cu and Al ions in the droplets when the droplets impinged on the heated substrate. SEM images of the most optimum sample is consisted of uniform grains with film thickness of ~1.9 µm. UV-Vis spectroscopy revealed that the film have energy gap of 3.54 eV with transparency above 60 % at visible light range. The conductivity of the film was 0.354 Scm^{-1}. The film showed the rectifying nature of diode in a junction of p-type $CuAlO_2$/n-type Si with turn on voltage around 0.4 eV. Under various illumination of incandescent lamp, the diode showed photoelectric effect.

CHAPTER I

INTRODUCTION

1.1. Introduction

Transparent conducting oxides (TCOs) are a class of materials which have attracted enormous attention from researchers and scientists all over the world. This material offer unprecedented range of applications for many exciting devices that requires both transparency and conductivity properties. Examples are to be used in devices like photovoltaic (Beyer *et al*., 2007), flat panel displays (Lee *et al*., 1997), and in light emitting and detecting photodiode (Kovac *et al*., 2003).

As the name signifies, TCOs are materials which are transparent and electrically conducting. Finding a material with both properties is very challenging since highly conductive material tends to be metallic whilst high transparent material is often an insulator. However, several ceramic metal oxides are found to have a combination of being conductive yet transparent. TCOs which are widely used now are the n-types like In_2O_3:Sn, SnO_2, Cd_2SnO_4 andAl:ZnO (Banarjee *et al.*, 2003 and Choi *et al*., 2007). P type TCOs have also been reported especially those that are based on cuprate oxides. P-type, transparent delafossite $CuAlO_2$ was first reported by Kawazoe *et al*., (1997). With the discovery of this $CuAlO_2$, the realization of transparent p-n junctions for the creation of transparent semiconducting devices will be possible.

Apart from cuprate based oxides, there are not many transparent oxides which are reported to be hole conducting and at the same time transparent. In most oxides, electronegativity of oxygen 2p orbitals lead to the formation of deep valence band maximum (VBM) therefore hole are localized around the oxygen atom. Moreover hole doping is rather difficult as well. To overcome the strong localization, Kawazoe *et al*., (1997) suggested on the modification of the energy band structures of several metal oxides to reduce the deep hole traps due to oxygen. This can be done by introducing cationic elements which have d^{10} closed shell with energy comparable to the oxygen 2p level. The closed d shell is also preferred to be used due to the coloration of open d shell which may induce the transparency of the films (Buljan *et al*., 2001). There are several metal oxides that can be created following this band modification model. The oxides are centered on the cuprate based with $CuAlO_2$ as leading candidate. To date $CuAlO_2$ films have been made by various methods: physical and chemicals. The formation of film at low temperature using chemical methods is desired. Low temperature process is desired as it will widen the choice (even on polymer), reduce interface reaction and cost effective.

1.2. Problem Statement

Since Kawazoe et al. discovered p type conduction in $CuAlO_2$, several studies on the stoichiometry and preparation techniques of a single crystalline $CuAlO_2$ have been made. Evaluation on the thermodynamics and kinetic stability of $CuAlO_2$ by solid state reaction of CuO and α-Al_2O_3 annealed in air at 1200 °C shows the presence of $CuAlO_2$

(Kumekawa *et al*., 2009). And, at lower temperatures, CuO and $CuAl_2O_4$ co-exist (Shy and Tseng., 2005). The existence of $CuAl_2O_4$ has also been reported in sol-gel derived film using nitrate precursor after been annealed at 800 ºC (Salavati-Niasari *et al*., 2009). $CuAl_2O_4$ and CuO are said to be stable at 625°C to 1100°C (Jacob and Alcock., 1975). And $CuAlO_2$ only can be formed at 1050-1200°C. At elevated temperature >1200°C the stable $CuAlO_2$ may decompose (Kumekawa *et al*., 2009). There is only exist a small window at which $CuAlO_2$ can be formed. High deposition temperature limits the use and choice of substrate. Amorphous $CuAlO_2$ can be prepared by sputtering and the properties of the amorphous film are generally acceptable: transparency above 75 % in the visible region but with energy band gap of 1.6 eV. The room temperature electrical conductivity of the $CuAlO_2$ film is 0.32 Scm^{-1} (Chattopadhyay *et al*., 2007). Amorphous $CuAlO_2$ can be formed at much lower temperature.

Chemical spray deposition (CSD) process (CSD) is a versatile technique to form $CuAlO_2$ film on various substrates. CSD process can be done via spin coating, dip coating, and spray coating to produce the thin film. Spray coating can be done by spray pyrolysis technique. It has advantages over any physical methods are in term of simplicity and cost effectiveness. The operation of equipment is easy enough and applicable to extensive variety of precursor and substrate (Rim *et al*., 2002). In 2005, Bouzidi *et al*., (2005) had successfully produced a thin film $CuAlO_2$ by ultrasonic spray pyrolysis (USP) using chloride precursors on a glass substrate at substrate's temperature in the range of 450 to 525 °C. The amorphous $CuAlO_2$ films were transformed to crystalline $CuAlO_2$ after annealing at 570 °C. The films had band gap energy reported in

the range of 3.34 to 3.87 eV (Bouzidi *et al*., 2005). It is known that there are several parameters in the USP which will determine the final properties of the film produced. One of them is the acidity level of the starting precursor. This effect of pH was studied and reported by Singh *et al*., (2008) by varying the concentration of the HCl in the chloride precursors the pH was altered. Nonetheless the films produced were not very smooth, in fact were very inhomogenous (Singh *et al*., 2008). Chloride precursor may not be the best of precursor to form smooth $CuAlO_2$ film. The inhomogenity could be due to the presence of Cl_2 gas formed during the spray coating process. Prior to the report by Singh et al, Toonoka et al., (2002) investigated on the effect of chloride, alkoxide, nitrate and a mixture of these precursors to the properties of $CuAlO_2$ film made by CSD via dip coating. They reported on the superiority properties of the films produced by using nitrate precursor as nitrate derived films were much more crystalline, smoother and has better conductivity. To date, no work has been reported on the use of nitrate precursor for $CuAlO_2$ film formed by USP. Therefore, it is of interest to study the quality of films formed by USP via nitrate route.

In this work, $CuAlO_2$ thin films were produced by USP using nitrate precursors (nitrate route) on silicon. As mentioned nitrate precursors were used due to their advantages over the chlorides such as less aggressive and corrosive hence film formed may have much better homogenity (Perednis., 2003). The deposition parameters were investigated aiming at the formation of coating with desired phase at lower temperature. Lower temperature process can be achieved by USP as the process occurs by ionic reactions within droplets. Having achieved an optimum $CuAlO_2$ films, the properties

especially the diode properties were studied. To date, not much have been reported on the diode properties of $CuAlO_2$ film. In this thesis, photodiode properties of transparent $CuAlO_2$ film on n-type silicon are presented.

1.3. Objective of the Research

The main objectives of this research are:

1. To produce $CuAlO_2$ films at lower temperature by USP using nitrate precursor.
2. To investigate the effect of the deposition parameters to the properties of the films especially the morphology, optical and electrical properties.
3. To characterize the diode properties of the $CuAlO_2$ films formed by USP on n-type Si especially under illumination.

1.4. Scope of Study

The study encompasses on the formation of p-type $CuAlO_2$ thin films at lower temperature by USP technique on an n-type (100) Si. The precursor was Cu and Al nitrate salts were dissolved in appropriate solvents. The deposition parameters were explored as to get an optimum condition to produce $CuAlO_2$ film with good coverage uniformity, and crystalline.

In this work X-Ray Diffraction (XRD) and Raman Spectroscopy were used to characterize the phase present. Scanning Electron Microscopy (SEM) and Atomic Force

Microscopy (AFM) were used to characterize the surface morphology of the films. Ultraviolet/Visible Spectroscopy (UV-Vis) and Photoluminescence (PL) were used to characterize the optical properties of the films. To assess the diode properties of the films on silicon, Semiconductor Parameter Analysis (SPA) was used under illumination. Series of experiments were also done to characterize the photo response of the $CuAlO_2$ on silicon.

1.5. Thesis Structure

This thesis consists of five chapters. The first chapter is on the background, problem statement, research objectives, and the scope of this study. The second chapter is on the literature review related to the research. The third chapter provides the detailed methodology of this research. The fourth chapter presents the analysis and discussion of the research findings. The fifth chapter provides the conclusion and suggestions for future work.

CHAPTER 2

LITERATURE REVIEW

2.1. Introduction

Transparent Conducting Oxides (TCOs) have attracted vast attention across the world due to its tremendous applications in realizing transparent electronics circuit for the formation of transparent devices (Ohta and Hosono, 2004). The two special features that must be accomplished in TCOs are wide energy gap (band gap) between the material's conduction and valence band and high concentration and mobility of the electrical carriers. Figure 2.1 represents an oversimplified energy band diagram of a typical TCO. The band gap energy between the valence band and the conduction band must be considerably bigger than the incoming energy of the visible light (photon). If the material exhibit this, visible photon will only pass through the material without any adsorption of the energy. The band gap of TCOs has to be greater than 3.1 eV to allow light with energy of 2-3 eV (visible red to blue light) to pass through the material (Thomas, 1997) .

However, highly transparent material is always associated with being insulating with high electrical resistance. To create a material with high electrical conductivity, free electrons are needed in the conduction band or free holes in the valence band. Free electron can be created by excitation of electrons from the valence band to the conduction band. But as mentioned, TCOs must have high energy gap and this limits the

generation or the excitation process by photon absorption. Generation due to heat energy is possible to excite electrons in the conduction band.

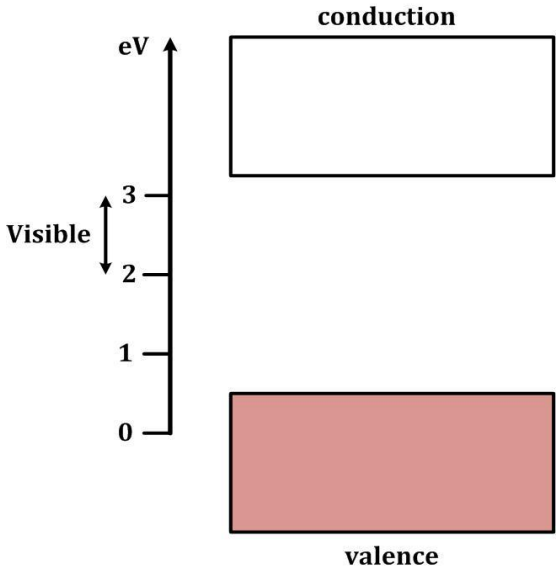

Figure 2.1: A schematic band energy levels of a typical Transparent Conducting Oxide (TCO) (Thomas, 1997)

Equation 2.1 shows the relationship of conductivity, σ with the number of free electron, N, and the mobility μ of an electron. Based on this equation, σ can be increased when N and μ are increased. N depends on the excitation process and is band gap dependent.

$$\sigma = N\mu e \tag{2.1}$$

Therefore, to reduce resistivity the carrier mobility of the carrier charge must be increased if N cannot be increased too much. As mentioned, TCOs are oxide semiconductors. The conductivity is dependent on either p or n. To get transparency, the

band gap must be > 3 eV as to allow photons with λ= 300-500 nm to transmit. Resistivity is often $\rho < 10^{-3}$ Ωcm, with degenerate carrier density $\geq 10^{20}$ cm^{-3} and the hall mobility $\mu \geq 62.5$ $cm^2V^{-1}s^{-1}$ (Calnan and Tiwari, 2010). Generation of electron or hole is dependent on intrinsic nature of the semiconductor as well. The μ is dependent on the scattering events in the semiconductor and is largely dependent on the morphology, crystallinity and impurities.

2.2. Transparent Conducting Oxides (TCOs)

2.2.1. N-Type Semiconductor

There are several n-type TCOs materials that have been used in electronic industries. They are often used as transparent electrode for optoelectronic devices. N-type TCOs have resistivity of $< 10^{-4}$ Ω cm and overall transmittance of above 80 % at the visible photon range. Several n-type TCOs have been successfully synthesized with resitivity below 1.6 x 10^{-4} Ωcm, for example Al-doped ZnO (Al:ZnO) thin films deposited by pulsed laser deposition (PLD) technique (Agura, 2003). Al:ZnO produced by sputtering technique on the other hand has been reported to have resistivity of 1.39 x 10^{-4} Ωcm (Cao *et al*., 2004).

Indium tin oxide (ITO) [In_2O_3 : Sn) is perhaps the most used n-type TCO. ITO deposited by PLD on a glass substrate has a reported resistivity value of 0.9 x 10^{-4} Ωcm (Choi *et al*., 2003). ITO can also be sputtered to produce film with resistivity of ~ 10^{-4} Ωcm (Ray *et al*., 2007). However, it is believed that a shortage of indium may occur in

the near future. Moreover, the price of indium has increased drastically, thus indium free TCOs are being sought after (Minami, 2008). Moreover, indium is toxic and hence is harmful to human. Al:ZnO can be used to replace ITO as TCO for electrodes. ZnO is a material that can easily be obtained or synthesized.

Another well known n-type material is fluorine doped indium oxide (F : In_2O_3 or IFO). Thin IFO film has been reported to be produced by spray pyrolysis with resistance of 120 Ωcm and transmittance of 88 % in the visible length (Rozati *et al*., 2004). IFO has been reported by pyrosol method with good properties to be used as electrode for solar cell (Untila *et al*., 2009).

Recently, new semiconductor materials consist of muticomponent oxides such as ternary compounds have been produced. For example, spray coated $MgIn_2O_4$ film have been reported to have electrical conductivity of 0.7 Scm^{-1} with overall transmittance of > 75 % at the visible photon range and also Hall mobility excess 1.5 x 10^{-3} $cm^2V^{-1}S^{-1}$ (Sanjeeviraja *et al*., 2010). Excess Mg in $MgIn_2O_4$ have been reported to have resulted in lowering the resistivity to 10^{-2} Ωcm (Lee *et al*., 2008). On the other hand, $In_4Sn_3O_{12}$ film deposited by sputtering has reported resistivity of 2 x 10^{-4} Ωcm, carrier concentration of ~ 10^{21} cm^{-3}, Hall mobility of 20 $cm^2V^{-1}s^{-1}$ and average transmittance of > 80% in the visible range (Minami *et al*., 1997).

The introduction of dopant metal to a conducting binary metal oxide is well studied to achieve higher conductivity TCOs. Dopant causes disorder to the band structure of the TCOs in which will cause localization of electron in the band structures

by introducing large number of carriers (Minami, 2005). But dopants are also scattering center that may reduce μ in the TCOs.

2.2.2 P-Type Semiconductor

P-type semiconductor is characterized by the existence of acceptor level in the band energy located close to the valence band that can induce hole formation. Holes are the majority carriers responsible for the conduction mechanism of p-type materials. Among the first p-type TCOs, Sato *et al*., (1993) reported on the NiO. However, stoichiometric NiO exhibits an electrical resistivity in the order of 10^{13} Ωcm. Its resistivity can be much lowered with the existance of nickel vacancies or interstitial oxygen. Normally, p-type conductivity is of the order magnitude smaller than in the n-type conductivity.

Apart from NiO, $Cu_2O$and CuO are among oxides exhibiting p-type conductivity. Figure 2.2 shows p-type TCOs materials (Banarjee *et al*., 2008). This figure displays all of the important hole conducting TCOs and will be explained in here.

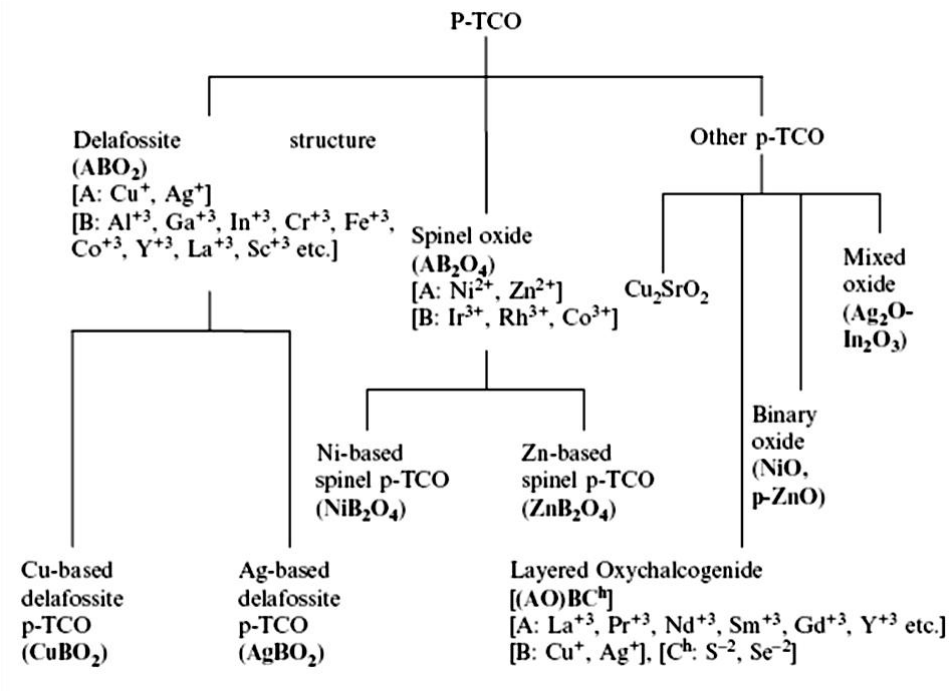

Figure 2.2. P-type of transparent conducting oxides that have been produced at the present (Banerjee *et al*, 2008).

It is best to first describe on the origin of the hole conductions in p-type TCO. As mentioned, the conductivity in p-type TCOs is much less then n-type TCOs. One of the reasons for high resistivity is on the lack of free holes available in p-type TCOs. Another reason is the mobility of holes is known to be much smaller than that of electrons. The lower conductivity of p-type is often attributed to the deep traps of highly electronegative of oxygen atoms thus localizing the hole at the valence band edge of oxide. As the holes are not delocalize, they are not free to move. To overcome this problem, cation with closed d-shell can be used to create a delocalization of the holes, as shown in Figure 2.3 (Kawazoe *et al*., 2005).

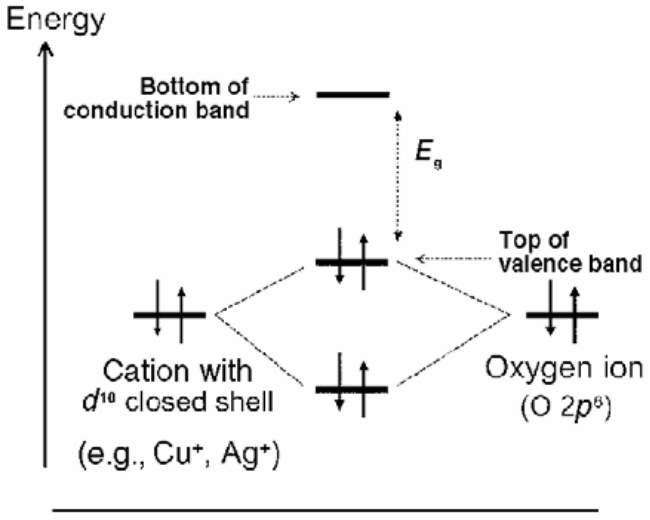

Figure 2.3. The schematic of diagram band which show the chemical interaction between oxide ion and cation with d-close shell electronic configuration (Kawazoe *et al*, 2005)

As seen in Figure 2.3, the localization from oxygen atom can significantly be reduced by the modification of the cation with d^{10} closed from the metal such as Ag and Cu. More dispersive bands with lower effective mass have been pushed up above the non bonding O 2p or Cu 3d by the interaction of metal with some O 2p state (Sheng *et al*., 2006).

Generally there are two main p-type TCOs, that are delafossite and non delafossite oxides (Figure 2.2). The non delafossite TCOs are spinel and other types. In the other types class, $SrCu_2O_2$, layered oxychalcogenide and binary oxide like NiO and mixed oxide are listed. In spinel oxide, there are Ni based and Zn based.

2.2.2.1. Spinel Oxide

The group of material known as spinel has the general formula AB_2O_4 with A is a divalent metal such as Mg, Mn, Cu, Zn, Cd, Pb, Co, Ni whereas B is a trivalent metal such as Al, Cr, Fe, Co. The structure of the spinel is given in Figure 2.4. A atoms are located at the point of a diamond type structure while the other atom are distributed around them. Each of the A atom is surrounded by four equidistant, tetrahedrally disposed oxygen atoms as shown in the Figure 2.4i. Meanwhile, for each B atom, around them are six oxygen atom at the corner of octahedron shown in the Figure 2.4.ii. Each oxygen atom is surrounded by three equidistant B atoms and one A atom.

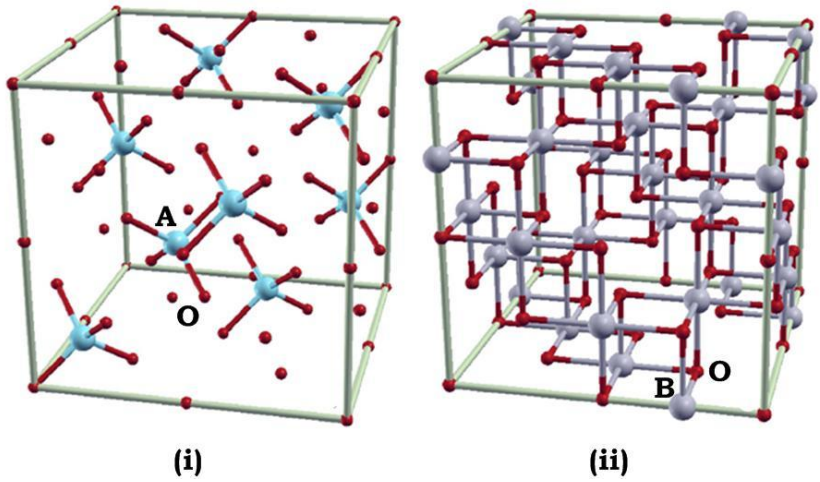

Figure 2.4. Atomic structure of AB_2O_4 spinel showing the position of A and B atoms around oxygen (Segev *et al*, 2005)

In the spinel structure, the atomic structure is not divided into AO and B_2O_3 groups or into A and BO_2 ions. The whole crystal is a single molecule where each atom

is held by single bonds to those adjacent. Therefore, the empirical formula AB_2O_4 is the only formula which correctly represent the structure of this substance (Huggins, 1923).

The spinel $CuAl_2O_4$ thin film can be deposited by sputtering. Post heat treatment of the films increase their crystallinity. $CuAl_2O_4$ have been synthesized by sol-gel and reported to have a band gap E_g value of = 2.10 eV (Salavati-Niasari *et al*., 2009). As seen in Figure 2.2, the p-type TCOs can be spinel oxide, Ni based or Zn based. Examples are NiB_2O_4 and ZnB_2O_4 respectively.

2.2.2.2. Non Delafossite : Cu_2SrO_2

$SrCu_2O_2$ has tetragonal crystal structure with lattice parameter of a=5.48Å and c= 9.82 Å. The origin of p-type behavior in this material is resulted from +1 of Cu cation. This material can be formed at considerably low temperature and has kinetics stability (Varadarajan *et al*., 2005). Furthermore, $SrCu_2O_2$ is built up by Cu-O chain along to the [100] and [010] direction in one dimensional, zigzag architecture with θ=96.3 (Papadopoulou *et al*., 2008).

Cu_2SrO_2 is one of a few non delafossite p-type TCOs which has a potential for optoelectronic applications (Sheng *et al*., 2006). The crystal structure of Cu_2SrO_2 is tetragonal with space group of $I4_1$/amd as shown in the Figure 2.5. The lattice parameters of Cu_2SrO_2 are a= 5.48 Å and c= 9.82 ° respectively. The crystal structure of Cu_2SrO_2 is consisted of Sr atoms located at the center of distorted octahedron formed by O atoms. The Cu atoms hold by O atoms to forms O-Cu-O dumbell configuration. This

dumbell may similar to Cu_2O as shown in Figure 2.5 (i) therefore this Cu_2SrO_2 can be considered to be derived from the Cu_2O_2. However the discrepancy of those dumbell structure is in Cu_2O the dumbell is built three dimensionally whilst in Cu_2SrO_2 the dumbells arrangement is one dimensional zigzag chains along the c and b axis orientation (Nie *et al*., 2002). Note that Cu_2O is also p-type conducting.

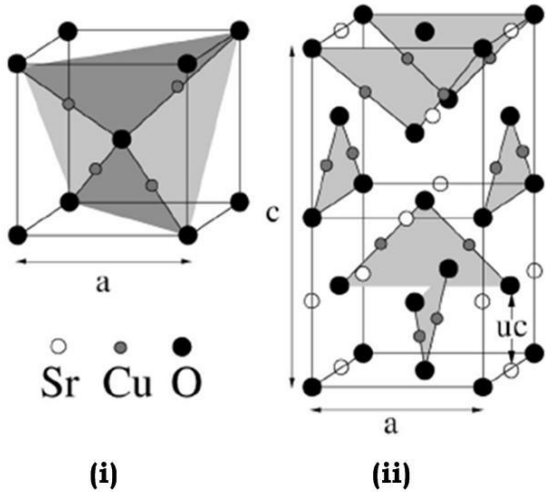

Figure 2.5. Crystal structure of Cu_2O (i) and Cu_2SrO_2 (ii)

Not many works on the synthesis of Cu_2SrO_2 have been reported so far. However, in 2003 Roy *et al* reported on the deposition of Cu_2SrO_2 thin film by spraying and PLD. The films deposited by spraying method have to be treated by post annealing in order to obtain pure Cu_2SrO_2 phase whilst the film deposited using PLD has a mixture of Cu_2SrO_2 with Cu_2O (Roy *et al*., 2003). The improvement of Cu_2SrO_2 formation by PLD was shown by Varadarajan *et al*., (2005) where they reported on the epitaxial growth of nearly pure phase of Cu_2SrO_2 at 500°C. MOCVD derived Cu_2SrO_2 thin film was also reported at temperature 480°C to 540°C. The as deposited film is consist of

mixture of CuO and $SrCO_3$ (Deschanvres *et al*., 2008). Cu_2SrO_2 can only be synthesized at low oxygen pressure.

2.2.2.3. Delafossite p-type TCO

Delafossite has hexagonal layered crystal structure with layers of AO_2 and A stacked alternately perpendicular to c-axis. The general formula of delafossite structure is $A^{+1}B^{3+}O_2$. As seen in Figure 2.6, delafossite consists of a rather distorted edge-shared BO_6 octahedra and closed packed A^+ cation planes to form linear O-A^{+1}-O dumbbells. The four cations that is one A^{+1} and three B^{3+} link the oxygen. Based on the stacking layer structures, the possible polytype may coexist are rombohedral "3R" which have arrangement structures AaBbCcAa whilst the hexagonal "2H" polytype consists of sequence arrangement AaBbAa… (Ingram *et al*., 2004). Nonetheless, there are no significant differences in the electrical properties between 2H and 3R since both had almost the same α-axis (Deng *et al*., 2009).

As mentioned and seen in Figure 2.2, there two type of p-type TCOs with delafossite structures: $CuB^{III}O_2$ and $AgB^{III}O_2$ where B^{III} is trivalent cation. Ag based delafossite oxides have large band gap of > 4.12 eV and transparency above 50 % (Vanaja *et al*., 2008). However, the Ag based delafossite is much more difficult to produce and it is unstable thermodynamically (Clayton *et al*., 2002). The Cu based will be explained in the next sub heading.

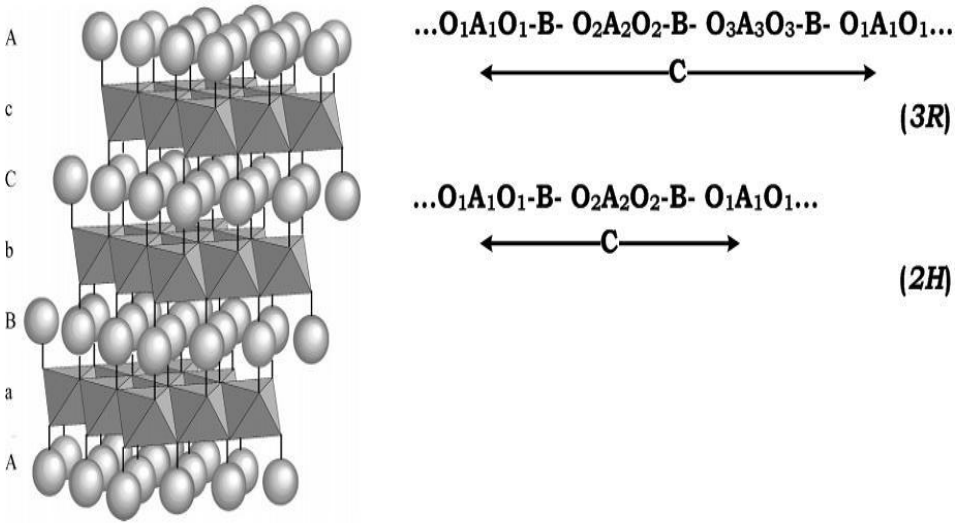

Figure 2.6. The concept of delafossite structures of 3R with the sequences of stacking AaBbCcAa along c-axis. For hexagonal 2H polytype, the stacking layer order is AaBbAb. The polyhedron and sphere represent BO_6 distorted octahedron and linearly coordinated A^+ cations (Ingram *et al*., 2004 and Doumerc *et al*, 1987).

2.3. Delafossite p-type $CuAlO_2$

$Cu^{I}M^{III}O_2$ has gained much interest as p-type TCOs. Apart from delafossite materials, Cu_2O and CuO are known to have holes conduction as well. The first report on the electrical conductivity of CuO is by Weichman where photoconductivity was reported to depend on the oxygen content in the CuO (Weichman, 1960). The energy band gap of CuO and Cu_2O are in the range of 1.7 to 2.2 eV (Kose *et al*., 2008). The small band gap value is one of the main reason underlay CuO and Cu_2O are not being considered as TCOs. These oxides are conducting but coloured. The small band gap of Cu_2O is assumed originate from the three dimensional interaction between electron $3d^{10}$ electron and neighboring Cu^+ ions. The dumbbell unit in Cu_2O connected three

dimensionally rather than connected preferentially parallel to c-axis with two dimensional layers sandwiched by AlO_6 octahedron similar to $CuAlO_2$. This controls the degree of mixing between O 2p and Cu 3d in the valence band vicinity. In Cu_2O, four Cu ion linked to each O ions. Thus, the interactions and mixing between O 2p and Cu 3d is rather smaller than those in $CuAlO_2$ and the valence band top of $CuAlO_2$ has smaller dispersion than Cu_2O. As a result the mobility and narrow gap in Cu_2O have been observed (Yanagi *et al*., 2000). Moreover, the strong coloration effect as reported by Richardson *et al*., (2001) which arise from the d^{10}—d^{10} interaction in this copper oxides encourage many researchers to find more materials with larger band gap as to increase transparency (Buljan *et al*., 2001).

P-type conductivity in delafossite oxides arise when there is a lack of metal cations or excess in oxygen within the crystal lattice. Defect chemistry therefore plays an important role in the determination of the final conductivity of the delafossite oxide (Koumoto *et al*., 2001). Excess oxygen and Cu or Al deficient will create more holes as written in (2.2).

$$O_2(g) = 2O^{o}_{x} + V_{Cu}' + V_{Al}''' + 4h^{*} \qquad (2.2)$$

In (2.2) V_{Cu}, O_o, V_{Al} and h are Cu vacancy, oxygen in oxygen site, Al vacancy and electron hole respectively. The superscript ^{x}, ‘, * refer to effective charge state for neutral, negative and positive of the vacancies and holes respectively. The presence of excess oxygen in the delafossite film changes the equilibrium formula of the compound which can be rewritten as $CuAlO_{2+x}$. As seen in (2.2), more oxygen creates more holes.

The schematic of excess oxygen in the lattice site and interstitial site in $CuAlO_2$ delafossite compound is shown in Figure 2.7 (Banerjee and Chattopadhyay, 2005). In this figure, (a) shows stoichiometric $CuAlO_2$ whereas (b) and (c) shows excess oxygen at different sites.

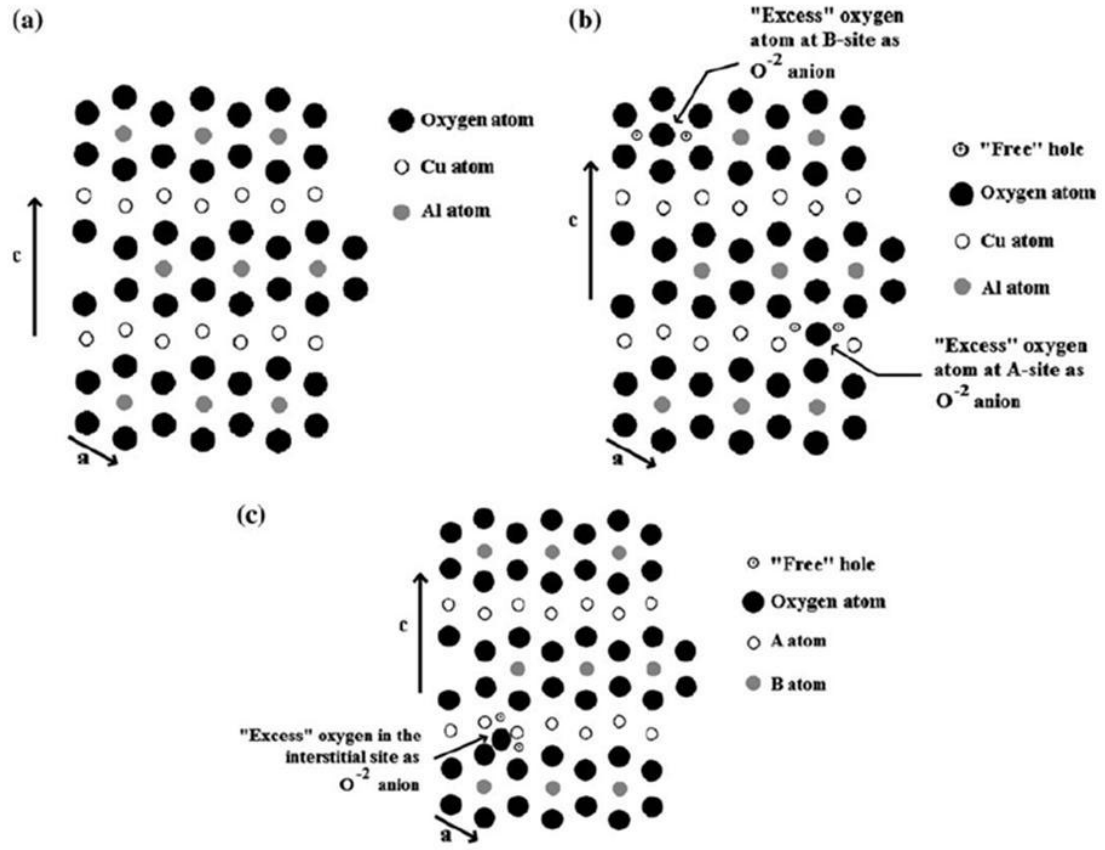

Figure 2.7. Schematic representation of $CuAlO_2$ at stoichiometric equilibrium state (a), nonstoichiometric state with surplus oxygen in the lattice site (b), and (c) nonstoichiometric state with excess oxygen in the interstitial site (Banerjee and Chattopadhyay, 2005)

According to Kawazoe *et al*., (1997) most metal oxides have strong localization at the upper edge of the valence band hence no free carriers exist. The modification of the energy band structure is therefore needed as to reduce the localization and to free more carriers. To do this, the cationic species must possess a closed shell with energy comparable to the energy of the 2p levels of the oxygen anion. The Cu^{+} has an electronic configuration of $d^{10}s^{0}$ where the energy of d^{10} closed shell will overlap to that 2p electron from the oxygen ions. The crystal structure is an important factor to be considered as well.

Tetrahedral coordination is a suitable candidate as there is a lack of oxygen bonding to the cation in the structure. This can further reducing the localization behaviors of the 2p electrons of oxide ion. In addition, lowering the dimension of crosslinking of Cu^{+} ions is required to widen the bandgap because of the direct interaction between d^{10} electrons on neighbouring Cu^{+} ions will reduce the band gap. As mentioned, energy gap > 3 eV must be achieved to get transparent oxide. Considering all of these requirements, Kawazoe had proposed $CuAlO_2$ delafossite structure one of the potential candidates for high conductive p-type TCO (Kawazoe *et al*., 1997).

$CuAlO_2$ has a rombohedral space group of R3m. In the structure, the Cu atoms are linearly linked to the oxygen atom with 2 fold coordination. Oxygens are coordinated 4-fold which comes from 3 fold by Al and 1-fold by Cu. Figure 2.8 shows the crystal structure of $CuAlO_2$ showing the layers of AlO_6 and Cu alternately stacked along c-axis.

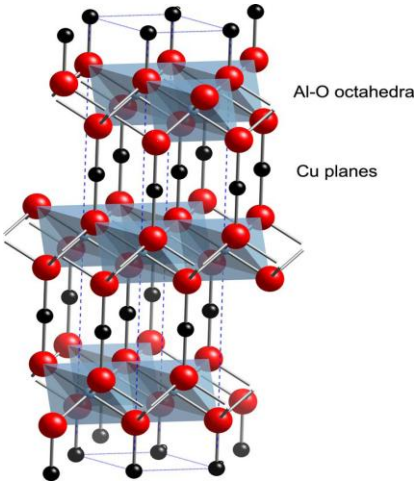

Figure 2.8. The crystal structure of $CuAlO_2$. The layers of AlO_6 and Cu are alternately stacked along c-axis (Tate *et al*., 2009).

2.4. $CuAlO_2$: Phase Equilibria

As described previously, the emphasis on the p-type TCOs has been focused on gaining understanding on what is the origin of the hole conduction and how increase the conductivity. In this context, apart from crystal structure, micro structural and phase purity of p-type TCOs must also be considered. A smooth, uniform $CuAlO_2$ is desired to avoid electron scattering and when used in optical application, light scattering is expected in a rough oxide. Processing and formation of $CuAlO_2$ as p-type TCO have therefore been focused in achieving smooth, pure $CuAlO_2$.

In here phase equilibria will be discussed as it is important to know on the conditions at which $CuAlO_2$ exist. Equations (2.3), (2.4), (2.5) and (2.6) for the formation of CuO, $CuAlO_2$ and $CuAl_2O_4$ (Jacob and Alcock., 1975).

$$2Cu_2O + O_2 \longrightarrow 4\,CuO \qquad \Delta G^\circ = -62{,}354 + 44.89T\ (\pm 100) \qquad (2.3)$$

$$4Cu + O_2 + 2Al_2O_3 \longrightarrow 4CuAlO_2 \qquad \Delta G^\circ = -91{,}510 + 39.21T\ (\pm 300) \qquad (2.4)$$

$$Cu_2O + Al_2O_3 \longrightarrow 2CuAlO_2 \qquad \Delta G^\circ = -5{,}670 + 2.49T\ (\pm 300) \qquad (2.5)$$

$$4CuAlO_2 + 2\,Al_2O_3 + O_2 \longrightarrow 4CuAl_2O_4 \quad \Delta G^\circ = -33{,}400 + 20.02T\ (\pm 300) \qquad (2.6)$$

Reactions 2.4 and 2.5 will only take place at high temperature of ~ 1100°C and 1200°C. Several works on the solid state reaction between CuO and Al_2O_3 has been reported for example Shy *et al*., (2005). Works on Cu reaction with Al_2O_3 at temperature 1200 °C also results the formation of $CuAlO_2$ (Lockman *et al*., 2009).

To study the equilibrium of $CuAlO_2$ phase, thermogravimetry and thermodynamic calculations have been employed. For example a mixture of CuO and Al_2O_3 followed by heating will results in the formation of $CuAlO_2$ by applying heat and pressure at a certain condition. The TG-DTA evaluation is shown in the Figure 2.9

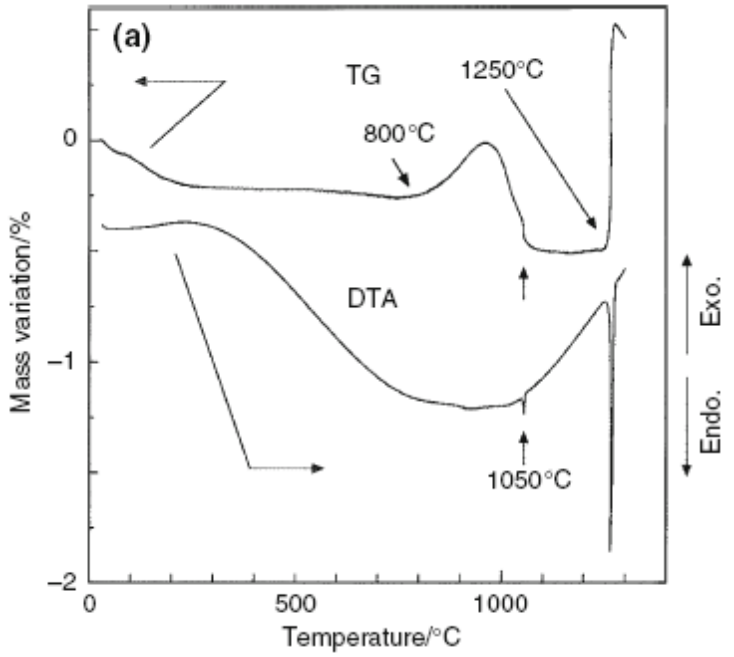

Figure 2.9. TG-DTA evaluation of $CuAlO_2$ (Kumekawa et al., 2009)

From Figure 2.9, the increase in mass at 800°C indicates a start of $CuAl_2O_4$ formation. Further heating to 950°C shows reducing of mass which indicate the formation of $CuAlO_2$ has started. The discontinuous mass decrease to 1050°C along with endothermic reaction attributed to the reduction of CuO converted to Cu_2O. The reaction from 1050°C to 1200°C is associated with the formation of $CuAlO_2$ with the reaction proposed in Equation 2.8. Furthermore, the endothermic peak at 1250°C is melting point of $CuAlO_2$ (Kumekawa *et al*., 2009). The reverse reaction also is studied by Kumekawa in which $CuAlO_2$ powder was calcined at 900°C for about 12 hours in air. The result shows that $CuAlO_2$ is thermodynamically instable at temperature lower than 800°C with the reaction proposed as shown in the equation (2.7).