

CHAPTER 1

INTRODUCTION

The quest and need for clean and economical energy sources have received much attention of both technological and academic researchers. The aim of research and development in energy sector is to reduce the energy cost. There is a steady increase in the expenditure of energy resulting from the effect of man's continuous struggle to survive. We consume energy in the form of food, clothing, shelter and tools, and use energy for transportation, heating, cooling and entertainment. Since the present dependence on fossil fuels will be depleted in the long run, no country can depend on these indefinitely. One aspect that must be considered in connection with the energies of the future is pollution and possible measures to prevent it. This is especially true for nuclear generating plants. These factors, coupled with the increasing world population, create a need for more energy than traditional energy sources can supply. Solar energy utilization will play a great role in solving the world's energy needs of the future. The direct conversion of sunlight to electricity is likely to be a prime method of the future. In operational practice, solar cells have an advantage over thermal conversion modes. A solar cell responds linearly to the flux. There is no inertia to a solar-cell system, it immediately produces its output at the level appropriate to the solar intensity. Solar thermal systems need time to reach operating temperature. Fuel transport and storage problems are eliminated in a photovoltaic-power system. Solar energy can also be efficiently stored in batteries. The future development of photovoltaic cells, such as silicon, is hampered by the present cost of the materials and fabrication. In practical, direct conversion of solar energy to electrical energy and chemical energy using semiconductor photoelectrodes has attracted attention for many decades. The most

important components of a solar cell are the semiconductor materials that constitute the p-n junction. Among the two semiconductors, the p-type material is called as the absorber generator since it absorbs the solar radiation and generates the electron-hole pairs. Some of the leading absorber materials are Si, InP, GaAs, CdTe, CuInSe₂, Cu₂O etc.

Silicon is one of the most favoured materials because of its abundant availability and non-toxic nature. The major disadvantages of silicon solar cells are the requirements of high grade material and the problems associated with producing single crystals over large areas.

InP is potential candidate to be used as absorber for solar cells due to the high absorption coefficient and the band gap is very close to the optimum value. The main disadvantage of InP are processing method is not cost effective and the resources for indium is very limited.

GaAs is another promising material. The advantage of the GaAs based cells is that they can be operated at higher temperatures and have higher radiation resistance. One of the greatest advantages of GaAs and its alloys as PV cell materials is that it's amenable to a wide range of designs. A cell with a GaAs base can have several layers of slightly different compositions. The greatest barrier to the success of GaAs cells has been the high cost of single crystalline GaAs substrates. For this reason, GaAs cells are used primarily in concentrator system. For mass production of GaAs solar cells, gallium element availability and the toxic nature of the arsenic are considered as major limitations of this technology.

CdTe is another promising material for fabrication of cost effective and stable solar cells. The main obstacles regarding this material are the problems of doping, post deposition treatment and providing low resistance contacts.

CuInSe₂, one of the suitable material for solar cell production inspite of few minor problems regarding reproducibility and fabrication of large area solar cells.

Cu₂O is one of the most inexpensive and available semiconducting material for terrestrial solar cell applications due to the following reasons.

- (i) It has a direct band gap of 2.0 eV, which is within the acceptable range for solar energy conversion.
- (ii) Low cost, non-toxicity and the natural abundance of the base material.
- (iii) Cu₂O films have high optical transparency with a slightly yellowish appearance and absorb usually at wavelength below 600 nm.
- (iv) The Hall mobility of Cu₂O is usually larger than 10 cm²/Vsec in spite of the low formation temperature.
- (v) It has a high absorption coefficient in the visible region.
- (vi) The theoretical energy conversion efficiency of Cu₂O solar cell is of the order of 20%.
- (vii) Production of large area devices with Cu₂O is possible.
- (viii) Excitons created in Cu₂O have been shown as a suitable candidate for Bose-Einstein condensation.

- (ix) The nature of the p-type conductivity of Cu_2O is originated from the presence of Cu vacancies, which form an acceptor level above the valence band.
- (x) Cu_2O is a basic compound forming superconducting materials.
- (xi) It has the relatively low activation energy of 0.14 eV.
- (xii) The production cost of Cu_2O in thin film form is relatively low.
- (xiii) Low resistance is possible in Cu_2O by proper doping.

Cu_2O is one of the oldest semiconducting materials known to solid-state physicists. It has a historic significance for semiconductor physics, since the existence of holes was first discovered in it. It is one of the metal oxide semiconductors exhibiting p-type conductivity. Various devices have been fabricated using Cu_2O . Cu_2O films find diverse field of applications, such as absorber layer in thin film heterojunction solar cells [1-8], gas sensors [9-12], electrochromic devices [13-15] and optoelectronic devices [16].

It is generally believed that p-type conductivity in Cu_2O is due the existence of excessive oxygen (O) atoms beyond stoichiometric value. The amount of such excess of oxygen atoms in the films can be varied by proper preparation conditions. Such films prepared at optimized deposition conditions are highly applicable for various device applications.

Cu_2O is a p-type semiconductor having a band gap of 2.0 eV with cubic crystal structure as shown in Fig.1.1, the lattice parameter 'a' = 0.427 nm with high optical absorption coefficient in the visible range (350 – 800 nm).

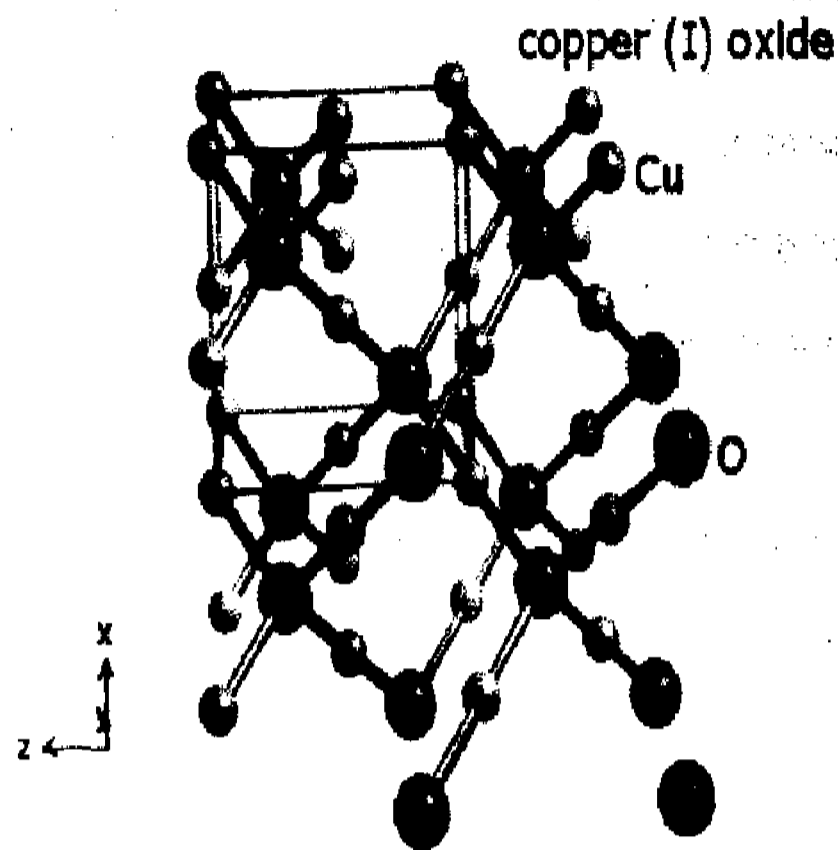


Fig1.1 Crystal structure of Cu_2O (Ref: webelement.com)

On the other hand, defect chemistry plays an important role in making the metal oxides either p- or n-type. Due to their optical and electrical properties, metal oxide semiconductor films have been widely studied and have received considerable attention. Transparent conducting oxides (TCOs) have been studied extensively because of their broad range of technical applications such as transparent electrodes in flat panel displays, solar cells, light emitting diodes, heat mirror coatings, varistors, acoustoelectric devices, photothermal conversion systems, phototransistors, photodiodes, gas sensors, liquid crystal displays, energy efficient windows, optical memories, electrochromic windows, ultrasonic oscillators and touch panels [17-28]. TCOs have high transmittance in the visible region and reflectance in the IR region. Because a TCO must necessarily represent a compromise between electrical conductivity and optical transmittance, a careful balance between these properties is required. In general, most of the known TCOs are n-type materials such as SnO_2 , In_2O_3 , CdO , ZnO , Cd_2SnO_4 , ZnSnO_3 , MgIn_2O_4 , $\text{Zn}_2\text{In}_2\text{O}_5$

[29-36]. For transparent semiconductor devices, p-n junction should be required as a combination of the two types of TCOs, but the corresponding p-type counterpart was surprisingly missing for a long time. Upto now, only very limited p-type transparent conducting oxide thin films have been fabricated. Most of these films showed either low conductivity or low transmittance. For example ZnO doped with nitrogen had a conductivity of 10^2 S cm^{-1} , and colour was brown [37]. $\text{In}_2\text{O}_3\text{-Ag}_2\text{O}$ had a conductivity of $10\text{-}10^3 \text{ S cm}^{-1}$, with a low average transmittance of 20 % in the visible range [38]. Recently Kawazoe et al. [39] reported the synthesis of transparent p-type semiconducting delafossite CuAlO_2 thin films. The realization of p-type TCOs is a milestone to expand the utilization of TCOs as transparent semiconductors, because a wide variety of active functions of semiconductor elements come from p-n junctions. P-type transparent conductive oxides have potential applications in photovoltaics, transparent electronics and organic opto-electronics [40]. This has opened up a new field in device technology in transparent electronics. Recently several p-type TCOs such as CuAlO_2 [41], LaCuOS [42] and LaCuOSe [43], CuGaO_2 [44] and $\text{SrCu}_2(\text{O})_2$ [45], NiCo_2O_4 [46] are developed and used in device fabrication. Among these p-type materials Cu_2O based ternary compound of CuAlO_2 is an important material. Apart from these, it can also be used as a good thermoelectric material [47]. Combining of all these properties, CuAlO_2 become an important material in the last few years. CuAlO_2 is delafossite $\text{Cu}^I \text{M}^{\text{III}} \text{O}_2$ class of materials where M^{III} is a trivalent cation, CuAlO_2 has the delafossite structure and belongs to the rhombohedral space group of $R\bar{3}m (D_{3d})$ (Fig.1.2) with optical band gap of 3.5 eV. Structure of CuAlO_2 delafossite had been extensively studied by Ishiguro et al [48], where they proposed alternative stacking of Cu^I and layers of nominal AlO_2

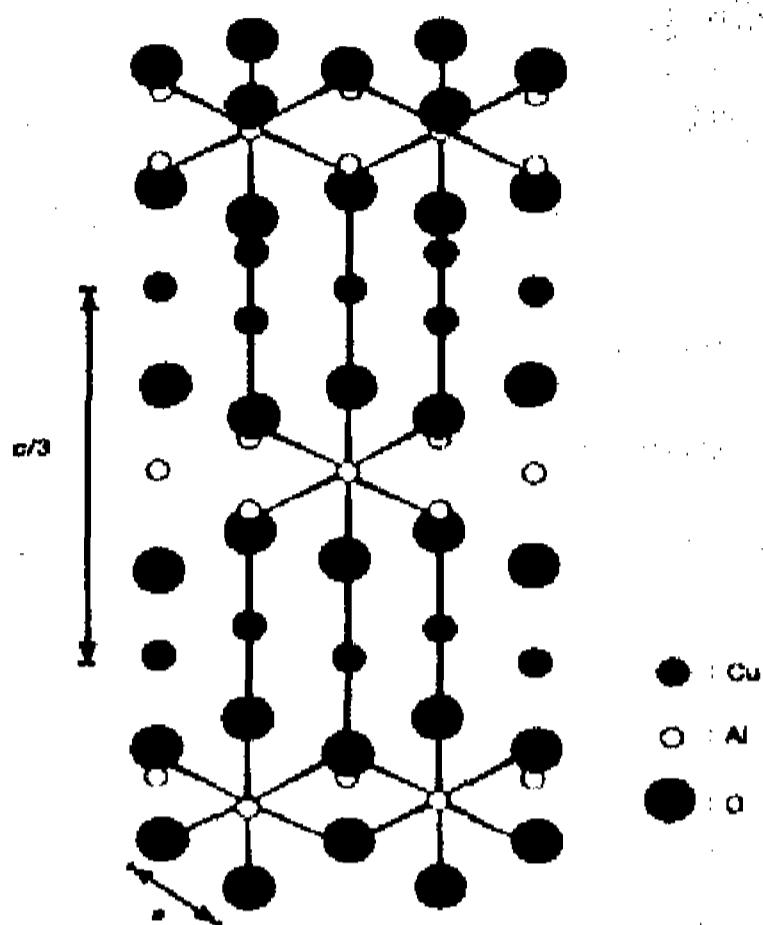


Fig.1.2 Crystal structure of CuAlO_2 delafossite consisting of stacked layers of O-Al-O-Cu-O in this order along the c-axis (Ref. H. Kawazoe (1977))

composition consisting of AlO_6 octahedra sharing edges. Each Cu atom is linearly coordinated with two oxygen atoms to form a O-Cu-O dumbbell unit parallel to the c-axis. O-atoms of O-Cu-O dumbbell lines all Cu layers with the AlO_2 layers.

REVIEW OF LITERATURE

This section presents an overview of the work reported on Cu_2O and CuAlO_2 films prepared by various deposition methods.

1.1 Cuprous oxide films

Various thin films deposition techniques such as electrodeposition [49- 64], chemical vapor deposition [65-66], activated reactive evaporation [67-68], solution growth [69-70], thermal oxidation [71-74], pulsed laser evaporation [75-77], filtered

cathodic vacuum arc deposition [78], sol-gel method [79-81], sputtering [82-95], molecular beam epitaxy [96], plasma evaporation [97] and galvanostatic deposition [98] etc. were employed for the preparation of Cu_2O films.

Liu et al [49] prepared Cu_2O films by electrodeposition on to InP (001) single crystal substrates and found that the morphology of the Cu_2O films can be influenced by the electrolyte acidities and the films exhibited only the (002) and (004) peaks at room temperatures with lattice parameter of 0.4269 nm. Mathew et al [50] studied the influence of bath temperature on the energy gap of the electrodeposited Cu_2O films. The films showed direct transitions with energy gap of 2.50 eV at room temperature and indirect transitions were observed at temperatures 138, 248 and 443 K corresponding transition energies 1.99, 2.21, 1.87 eV respectively.

Mahalingam et al [51,52] deposited Cu_2O films by electrodeposition on copper and tin oxide coated substrates. The films were polycrystalline nature with single phase of (200) orientation. The SEM results showed that the grains were in four-sided pyramid shape with an average grain size of 50 nm at bath temperature of 70 °C. When the films annealed at high temperatures (150 –550 °C) in air for 30 min, the grain size was increased to 100 nm. The electrical resistivity of the films decreased from $10^7 \Omega\text{cm}$ to $10^3 \Omega\text{cm}$ when the films were annealed at 350 °C. The films showed Cu_2O phase with an optical absorption coefficient of 10^4cm^{-1} .

Georgieva and Ristov [53] formed Cu_2O films by electrodeposition on indium tin oxide substrates. The films exhibited (200) preferential orientation with an optical band gap of 2.38 eV. The ITO/ Cu_2O solar cells exhibited open circuit voltage (V_{oc}) of

340 mV and short circuit current density (J_{sc}) of $245 \mu\text{A}/\text{cm}^2$. Sebastian et al [54] reported that the substrate pretreatment highly influence the film properties. It was found that the Cu_2O films deposited on chemically etched substrates possessed better crystalline properties and optical characteristics than the Cu_2O films deposited on mechanically polished substrates.

Liu et al [55] studied the growth dynamics, structural and optical properties of Cu_2O films on different substrates of Si, ITO and Au surfaces by electrodeposition. The films grown on ITO substrates, exhibited four diffraction peaks related to (110), (111), (200) and (220) phases of Cu_2O . The films grown on Si substrates showed similar X-ray patterns, but have broader and weaker diffraction peaks. In case of Au substrates a sharp peak at (200) orientation was observed. The films formed on Au substrates exhibited larger grains. Wijesundara et al [56] fabricated a solar cell of ITO/ Cu_2O /metal (Al or Au) by electrodeposition. The cell exhibited a V_{oc} of 385 mV and J_{sc} of $0.2 \text{ mA}/\text{cm}^2$

Siripala et al [57] prepared Cu_2O thin films by electrodeposition on ITO coated glass substrates. They reported that the films showed polycrystalline nature with cubic structure. When the Cu_2O films annealed above 300°C , the films were decomposed and dark black CuO films were observed. As deposited films showed a grain size of $1.2 \mu\text{m}$ with direct band gap of 2.0 eV .

Rakshani et al [58,59] deposited Cu_2O films by electrodeposition on molybdenum substrates and studied the photoelectrical properties with semitransparent aluminum and gold top electrodes. The device with a gold top electrode exhibited a weak photovoltaic effect. The deposition of aluminum top electrodes exhibits a three fold increase in

resistivity. The films were highly oriented along the (100) plane parallel to the substrate surface. The optical band gap of the films was 1.95 eV and the resistivity in the range $10^6 - 10^8 \Omega \text{ cm}$.

Morales et al [60] formed Cu_2O films by electrodeposition on titanium substrates and studied the effect of film thickness on electrochemical properties. They found that the small or intermediate thickness films exhibited a good electrochemical response in the lithium cells with excellent columbic efficiency over repeated charge and discharge cycles. Tang et al [61] prepared Cu_2O films by electrodeposition on TiO_2 films. It was found that the bath temperature and pH value strongly influence on the composition and microstructure of the Cu_2O films. The resistivity of the films decreased from $2 \times 10^6 \Omega \text{ cm}$ to $1 \times 10^4 \Omega \text{ cm}$ when the films annealed at 400°C . The band gap of the films was 2.0 eV at annealing temperature of 200°C .

Mukhopadhyay [62] prepared the Cu_2O film by electrodeposition on copper substrates. The films exhibited strong orientation in Cu_2O phase when the bath temperature was 60°C with a current density of 1.4 mA/cm^2 . The films showed an electrical resistivity of $2.6 \times 10^3 \Omega \text{ cm}$ with activation energy of 0.79 eV at room temperature. Briskman [63] made the Cu_2O -Cu backwall photovoltaic cells by electrodeposition. The cell exhibited the V_{oc} of 380 mV and J_{sc} of $600 \mu\text{A/cm}^2$ with AM1 isolation.

Santra et al [64] prepared Cu_2O films by electrodeposition and reported that the films exhibited (110), (111), (200) and (220) orientations and the optimum pH value of the electrolyte solution to deposit the films is found to lie in the range 9.2 - 9.3.

Maruyama [65] prepared Cu_2O film by chemical vapour deposition on silicon single crystal substrates. The films exhibited single phase with (100) orientation at an oxygen pressure ≤ 2.13 kPa. The optical energy gap decreased from 2.5 eV to 1.8 eV with increasing the fraction of Cu^{+2} in the films. Ortiz et al [66] deposited Cu_2O films by chemical vapour deposition on fiberglass and found that at a deposition temperature of 320°C two clear peaks were observed at 2θ values of 36.4° and 47.3° corresponds to Cu_2O along (111) and (200) directions.

Balamurugan et al [67,68] prepared Cu_2O films by activated reactive evaporation and observed that the oxygen flow rate and substrate temperature highly influence the properties Cu_2O films. The films exhibited dominated Cu_2O phase along with weak CuO phase when the films formed at room temperature under different oxygen flow rates. When the films formed at a substrate temperature of 200°C with oxygen flow rate of 7.5 sccm, the crystallite size was 9 nm with optical band gap of 2.54 eV and refractive index in the range 2.16 - 3.81.

Ristov et al [69] prepared Cu_2O films by solution growth onto glass substrates. The films exhibited single phase cubic structure with a conductivity of $2 \times 10^{-3} \Omega^{-1}\text{cm}^{-1}$, and energy gap of 2.0 eV when the films were formed at a bath temperature of 70°C . Fernando and Wetthasinghe [70] prepared Cu_2O films by solution method. The films prepared with HCl solution exhibited smaller grain size (average grain size of 55 nm) compared to that of the sample prepared with CuSO_4 solution (average grain size of 1.5 μm).

Tabuchi and Matsumura [71] prepared Cu_2O films by thermal oxidation on quartz substrates. They observed that hydrogen exposure of the films reduce the excessive oxygen in Cu_2O and improve the film properties. Minami et al [72] fabricated $\text{ZnO}/\text{Cu}_2\text{O}$ and $\text{AZO}/\text{Cu}_2\text{O}$ films by oxidizing copper at high temperature. All n-ZnO/p- Cu_2O heterojunctions exhibited good rectifying current-voltage characteristics.

Musa et al [73] prepared Cu_2O films by thermal oxidation of copper sheets and observed that the films formed at an oxidation temperature of 1050 °C consist entirely of Cu_2O and those films formed below the oxidation temperature of 1040 °C gave mixed oxides of Cu_2O of CuO . Santucci and Picozzi [74] deposited Cu_2O films by thermal evaporation onto quartz slides and the reported optical band gap was 2.06 eV.

Kikuchi and Tonooka [75] prepared Ni-doped Cu_2O films by pulsed laser deposition and observed the single phase Cu_2O at annealing temperature of 600 °C. The mobility of Ni doped films increased from 10 cm^2/Vsec to 30 cm^2/Vsec with increasing the annealing temperature. Wautelet et al [76] formed Cu_2O films on glass and oxidized in air under irradiation by means of a scanned Ar^+ laser beam. It was found that the optical characteristics of the films mainly depend on the laser beam power density and the thickness of the initial copper films.

Tanaka et al [77] fabricated $\text{ZnO}-\text{Cu}_2\text{O}$ and $\text{AZO}-\text{Cu}_2\text{O}$ heterojunctions by pulsed laser deposition. An open circuit voltage (V_{oc}) of 0.4 V, a short-circuit current density (J_{sc}) 0.71 mA/cm^2 , a fill factor of 0.4 and an energy conversion efficiency (η) of 1.2 % were obtained in a $\text{AZO}-\text{Cu}_2\text{O}$ devices under AM2 solar illumination. The V_{oc} , J_{sc} , FF

and η obtained in AZITO-Cu₂O heterojunctions increased as the Zn/(Zn+In) atomic ratio was increased.

Gan et al [78] deposited Cu₂O films on Si (100) substrates by a filtered cathodic vacuum arc and found that the substrate bias significantly affects the surface morphology, crystalline phase and texture. The films have uniform cluster when formed at bias voltage of - 100V. The chemical composition was analyzed by XPS. The main peaks of Cu 2p_{3/2} were observed at 933.7 eV and 933.8 eV, the O1s peak was located at 529.8 eV.

Ray [79] deposited Cu₂O film by sol-gel method on glass substrates and observed that the baking temperature influences the films properties. The films prepared at a baking temperature of 360 °C exhibits (111) and (200) direction of Cu₂O phase. The CuO phase was observed at a baking temperature of 400 – 500 °C. The estimated optical direct band gap for Cu₂O films was 2.10 eV.

Yang and Zhu [80] prepared Cu₂O films by sol-gel process. XPS spectra revealed that Cu¹ 2p peak was observed at 932.55 eV and two O1s peaks were observed at lower energy of 530.3 eV and at higher energy of 531.7 eV and reported that the Cu₂O films have hollow spheres with polycrystalline cubic structure. The broad absorber peak was observed at 505 nm indicating the band gap of 2.60 eV. Armelao et al [81] formed Cu₂O films by sol-gel process at room temperature and subsequently heat-treated at different temperatures (100-900 °C) in air and observed that the composition and crystalline dimensions are mainly depend on proper choice of processing conditions. All films having average crystalline size lower than 20 nm.

Kamimura et al [82] deposited Cu_2O films by dc reactive magnetron sputtering on fused quartz glass plates or sapphire wafer and found that the sputtering power, oxygen partial pressure and substrate temperature were important parameters in controlling the films properties. When the films formed at an oxygen partial pressure of 20 mtorr, only Cu_2O phase was observed while at higher oxygen partial pressures (30 mtorr) CuO phase was observed. The higher substrate temperature of 400°C resulted in sharp diffraction peaks in the XRD patterns. The films exhibited Cu phase at higher sputtering powers. The films formed at a sputtering power of 0.35 W/cm^2 , the Cu phase was effectively eliminated and reported electric resistivity was $10^5\ \Omega\text{cm}$ with optical band gap of 2.0 eV . Richardson et al [83] prepared Cu_2O films by dc magnetron sputtering on $\text{SnO}_2:\text{F}$ glass substrates. They reported the electrochromic properties of Cu_2O films.

Yin et al [84] formed Cu_2O films by dc facing magnetron sputtering on Mg (011) substrate and found that the films deposited at a substrate temperature of 700°C , highly crystalline Cu_2O phase was observed in (011) and (022) directions. Lu et al [85] reported the hydrogen plasma treatment on the electrical properties of N-doped Cu_2O films by dc magnetron sputtering. The hole carrier concentration of N-doped Cu_2O films increased from $9 \times 10^{17}\text{ cm}^{-3}$ to $4 \times 10^{18}\text{ cm}^{-3}$ with hydrogen plasma treatment. The roughness of the films reduced by hydrogen plasma treatment.

Ogwu et al [86] prepared Cu_2O film by dc magnetron sputtering, and found that the thicknesses of the films were proportional to the applied forward power. At low forward powers (200 W), the films were highly transparent (80% - 90%). CuO phase was observed at a forward power of 800 W.

Ishizuka et al [87,88] fabricated polycrystalline n-ZnO/p-Cu₂O heterojunctions by rf magnetron sputtering. They suggested that the defect passivation was very important in the fabrication of polycrystalline ZnO/Cu₂O heterojunction devices. They observed that the hole density increased from 10¹⁵ cm⁻³ to 10¹⁷ cm⁻³ with nitrogen doping. The resistivity decreased with increasing the nitrogen flow rate and obtained minimum resistivity was 15.2 Ωcm.

The effect of substrate temperature on the properties of rf sputtered Cu₂O films was studied by Ishizuka et al [89]. The films formed at a substrate temperature of 500 °C exhibited a typical hole concentration of the order 10¹⁵ cm⁻³ with a Hall mobility of 60 cm²/Vsec. They also investigated and compared the effects of defect passivation by hydrogen treatment and cyanide treatment on the properties of the films and found that the optical and electrical properties of the films were improved by each treatment [90]. The effect of IV group dopants also influenced the structural and electrical properties of Cu₂O films [91].

Parretta et al [92] deposited Cu₂O films by rf magnetron sputtering on glass substrates and observed that the XRD phases of the deposited films strongly depend on the oxygen content in the sputtering gas. At an oxygen partial pressure of 0.08 Pa a single phase Cu₂O was obtained. At higher oxygen partial pressures > 0.15 Pa the CuO phase was observed. Pierson et al [93] prepared Cu₂O films by rf magnetron sputtering on glass and silicon (100) substrates. The reported electrical resistivity was 3×10⁴ Ωcm and optical band gap was 2.45 eV and 2.11 eV.

Ghosh et al [94] deposited Cu_2O films by rf magnetron sputtering on glass substrates and observed that the substrate temperature strongly influence the properties of the films. The deposition rate and grain size increased with temperature where as the surface roughness decreased with substrate temperature. The optical band gap increased from 1.7 eV to 2.04 eV with increasing the substrate temperature from 30 °C to 150 °C.

Klein et al [95] prepared Cu_2O films by dc diode sputtering on glass and silicon substrates and found that the electrical and optical properties change with the oxygen content in the films and reported that the optical band gap of the films changed from 1.5 eV to 2.6 eV with oxygen content.

Kawaguchi et al [96] prepared Cu_2O films by molecular beam epitaxy on optically polished (001) MgO single crystal substrates and observed that the phase transmission of CuO and Cu_2O was controlled by the flux ratio Cu/O^* and reported that the Cu_2O films were grown at Cu/O^* ratio of about 0.6 at 400 °C .

Santra et al [97] deposited Cu_2O films by plasma evaporation method on glass and quartz substrates. They studied the effect of annealing on the crystallographic properties and found that Cu_2O phase was changed to CuO phase after annealing. The films showed p-type conductivity before and after annealing with an optical band gap of 2.1eV.

Mahalingam et al. [98] prepared Cu_2O films by galvanostatic deposition on Cu and SnO_2 substrates and reported that the Cu_2O films were found to have simple cubic structure with preferred orientation of (200) with band gap of 1.99 eV. The electrical resistivity decreased from $5 \times 10^7 \Omega\text{cm}$ to $3 \times 10^4 \Omega\text{cm}$ with temperature in annealing.

1.2 Reported work on CuAlO₂

CuAlO₂ is a promising p-type transparent conducting oxide and finds in many applications for optoelectronics devices. Literature survey revealed that the CuAlO₂ films were prepared by employing various physical and chemical techniques such as pulsed laser deposition [39,99], dip-coating [100], spin-on technique [101], chemical vapor deposition [102-103], ion exchange [104], sputtering [105-111] and electron beam evaporation [112].

Kawazoe et al [39] deposited CuAlO₂ films by pulsed laser deposition on single crystal sapphire substrates and studied the structural, electrical and optical properties. The X-ray diffraction results showed that all films belongs to the R3m space group and the grain size was around 100 nm. The electrical conductivity at room temperature was $0.95 \times 10^{-1} \text{ Scm}^{-1}$. The films showed Hall coefficient of $+48.6 \text{ cm}^3 \text{C}^{-1}$ with carrier density of $1.3 \times 10^{17} \text{ cm}^{-3}$. Both Hall effect and thermoelectric power measurement revealed that the films exhibited p-type conductivity. The optical band gap was found to be 3.5 eV. Yanagi et al [99] deposited CuAlO₂ films by pulsed laser deposition on single crystalline sapphire substrates. The films exhibited both direct and indirect transitions with optical band gap of 3.5 eV and 1.8 eV respectively.

Tonooka et al [100] formed CuAlO₂ films on glass substrates by dip-coating from several kinds of precursor solutions containing metal alkoxides or nitrates. They observed that dominant CuAlO₂ phase was observed in films calcinated at a temperature of 1000 °C. The films showed better electrical and structural properties when the samples were prepared with the nitrate process.

Gao et al [101] prepared CuAlO_2 films by spin-on technique on glass substrates. The films showed an electrical conductivity of 2.4 Scm^{-1} , Hall mobility of $3.6 \text{ cm}^2/\text{Vsec}$, carrier concentration of $5.4 \times 10^{18} \text{ cm}^{-3}$, seebeck coefficient of $+203 \mu\text{V K}^{-1}$ with an optical band gap of 3.75 eV .

Gong et al [102] deposited CuAlO_2 films using chemical vapour deposition and studied the crystallographic structure. They observed nanocrystalline CuAlO_2 phase in the films. These films exhibited p-type conductivity. The carrier density was found to be $1.8 \times 10^{19} \text{ cm}^{-3}$. The films showed direct transitions with an optical band gap of 3.75 eV .

Wang and Gong [103] prepared CuAlO_2 films by plasma enhanced MOCVD on quartz substrates and studied the effect of annealing on the properties of CuAlO_2 films. The transmittance of the films increased from 45 % to 52% after annealing. As deposited films showed optical band gap of 3.57 eV and the band gap increased with annealing the samples at $350 \text{ }^\circ\text{C}$.

Dloczik et al [104] formed CuAlO_2 films by ion exchange from LiAlO_2 on SnO_2 : F coated glass substrates and conducted spectral photovoltage measurements. They found that, the films exhibited p-type conductivity. Strong CuAlO_2 reflections were observed in the films annealed at a temperature of $400 \text{ }^\circ\text{C}$. The films showed direct transitions with an optical band gap of 3.54 eV .

Banerjee et al. [105-108] deposited CuAlO_2 films by dc sputtering and studied the effect of oxygen partial pressure and substrate temperature on the properties of the films. They observed that post deposition annealing of the films in oxygen atmosphere controls

the p-type conductivity. They suggested that the excess oxygen with in the crystallinesites, improves the p-type conductivity of the CuAlO_2 films. Thermo electric power measurements revealed that the films exhibited p-type conductivity with seebeck coefficient of $+230 \mu\text{VK}^{-1}$. They found that the higher the conductivity of the films, the closer in its fermi level to the upper edge of the valance band. X-ray diffraction pattern revealed that in all the films, strong reflections were occurred along (006) direction. The films showed a maximum hole concentration of 10^{17}cm^{-3} . The films showed direct transitions with energy gap of 3.90 eV.

Tsuboi et al [109] deposited CuAlO_2 films by dc reactive sputtering. The films showed smooth surface morphology at post annealing temperature of 500 °C and exhibited low electrical resistivity of $10\text{-}10^2 \Omega\text{cm}$.

Alkoy and Kelly [110] prepared CuAlO_2 films by pulsed magnetron sputtering on glass microscope slides and found that the films showed a single peak at $2\theta \approx 37.50^\circ$ before and after annealing for 1h at 550 °C. Ong and Gong [111] deposited the CuAlO_2 films by reactive co-sputtering and observed that the transmittance varied from 20% to 80% depending on the aluminum content. The optical band was observed in the range of 2.9 – 3.3 eV.

Kim and Choi [112] prepared CuAlO_2 films by electron beam evaporation and studied the effect of water vapor pressure in wet-oxidation on electrical and optical properties of the films. The films showed the preferential (006) orientation. The optical band gap was estimated to be 3.96 – 4.20 eV and the hole concentration varied from 10^{20}cm^{-3} to 10^{18}cm^{-3} according with water vapor pressure.

Literature survey revealed that the properties of the films mainly depend on the method of preparation and the deposition conditions maintained. Moreover, the sputtering technique gives more stable and reproducible properties and very little attention was focused on the preparation and characterization of Cu₂O and CuAlO₂ films. Sputtering techniques also give device quality films. The deposition rate in sputtering techniques is high and this technique is industrially adoptable. Hence a systematic study was made in the present investigation in the preparation and characterization of Cu₂O and CuAlO₂ thin films using dc magnetron sputtering technique.

The main objectives of the investigation include,

- (i) Preparation of Cu_2O and CuAlO_2 films using dc magnetron sputtering technique.
- (ii) Optimization of the deposition parameters such as oxygen partial pressure, substrate temperature, sputtering power, sputtering pressure and substrate bias voltage for producing good quality films.
- (iii) Systematic physical characterization of the deposited films by studying the film composition, crystal structure, surface morphology, electrical and optical properties.

In chapter II, the preparation techniques used for the deposition of Cu_2O and CuAlO_2 and various characterization techniques used in the present investigation are described.

Chapter III deals with the presentation of results and its discussion. It consists of a detailed discussion on the influence of oxygen partial pressure, substrate temperature, sputtering power, sputtering pressure, and substrate bias voltage on the physical properties of Cu_2O films.

The results and its discussion on CuAlO_2 films are reported in chapter IV.

The conclusion drawn from the present investigations are summarized in the last chapter.

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