Chapter 3

Fabrication of Cuprous and Cupric Oxide Thin Films

3.1. Substrate-ITO

3.1.1 Introduction

In Solar cell, Indium Tin Oxide (ITO) acts as a transparent window layer, which means that it allows light to pass through it to the active light absorbing materials beneath. Transparent conducting oxides exhibit high optical transparency and outstanding electrical conductivity. ITO is one of the most widely used important transparent conducting oxides. The ITO electrode consists of indium (III) oxide (In$_2$O$_3$) and tin (IV) oxide (SnO$_2$), with typically 90% In$_2$O$_3$ and 10% SnO$_2$ by weight. ITO has been widely studied in the past three decades due to its special properties as a semiconductor. It has a high transmittance of 80% in the visible light range and also has an outstanding electrical conductivity. Also, it has been used as a transparent contact in advanced electronic devices like Light Emitting Diode, Photodiode, Phototransistor and Laser. Its high transparency is used to check the type n/p of the films to be deposited on it. It is used to improve the optical sensitivity of light detecting devices or quantum efficiency of light emitting devices. The direct optical band gap of ITO film is generally greater than 3.75 eV (Shabbir A. Bashar, 1998) but a range of values from 3.5 eV to 4.06 eV is reported in the literature (Fan et al., and Good Enough et al., 1977). It works as transparent window layer and also as an electrical contact layer, which serves as an ohmic contact to harvest photo-generated charge carriers from the light absorbing materials. ITO is used in Photodiodes as Schottky metal contact (Shabbir A. Bashar, 1998).
3.1.2. Physical Structure and Properties of ITO

Indium Tin Oxide is formed by substitutional doping of In$_2$O$_3$ with Sn which replaces the In$^{3+}$ atoms from the cubic bixbyte structure of indium oxide Sn and thus forms an interstitial bond with oxygen and exists either as SnO or SnO$_2$ accordingly it has a valency of 2 or +4 respectively. This valency state exhibits the conductivity of ITO. The lower valence state results in a net reduction in carrier concentration since a hole is created which acts as a trap and reduces conductivity. On the other hand, predominance of the SnO$_2$ state means Sn$^{4+}$ acts as an n-type donor releasing electrons to the conduction band. However, in ITO, both substitutional tin and oxygen vacancies contribute to the high conductivity and the material can be represented as In$_{2x}$Sn$_x$O$_{3-2x}$. ITO films have a lattice parameter close to that of In$_2$O and lie in the range 10.12 to 10.31Å (Nath et al., 1980).

Hence the high transmittance and low resistivity of ITO is preferred as the working electrode for this present work. Throughout the experiment the working electrode didn’t affect the quality of the film deposited and no adjustment was required in the deposition condition.

3.2. Electrodes

Working Electrode

For the deposition of both cuprous and cupric oxides thin films, ITO coated glass plate of 20mm×20mm×1.1mm with a sheet resistance of 10 ohms/sq was purchased and used as the substrate. For experimental purpose the plates are cut into 1cm×2cm stripes. Substrate cleaning plays an important role in the deposition of Cu$_2$O thin film in order to get a better deposition at the substrate. Before deposition the surface of the working electrodes are well cleaned by acetone and then ultra
sonicated for 30 minutes using Sonicator bath. Then the plate is rinsed with double distilled water and allowed to dry completely.

**Counter Electrode**

The function of the counter electrode is to convert ionic conduction in the electrolyte to electronic conduction by electrochemical reaction. The counter electrode or the auxiliary electrode is a platinum electrode. In order to avoid an interfacial reaction at the working electrode, platinum is selected since it does not produce substances by electrolysis. Platinum sheet of 3mm×3mm size is mirror polished and is enclosed in a glass tube. Current will flow between working electrode and counter electrode.

**Reference Electrode**

The reference electrode is a Saturated Calomel Electrode (SCE). The calomel electrode consists of mercury covered with mercurous chloride (calomel) in contact with a solution of KCl: Hg | Hg₂Cl₂ | Cl⁻. The electrode is filled with a saturated KCl solution (reduction potential- 0.2415V). Since reference electrode has a constant makeup its potential is fixed. Therefore it is well used to control the potential of the working electrode. In the three electrode cell the reference electrode should be placed very close to the working electrode to minimise the loss of voltage drop in the electrolyte between the working electrodes and counter electrode.

**3.3. Electrolyte**

Copper Sulphate Pentahydrate (CuSO₄.5H₂O) was used as a copper source. Tartaric acid (HOOC-CH(OH)-CH(OH)-COOH) was used as a chelating agent. It is known as a bidentate ligand capable of forming Cu (II) chelates in a wide pH region
(Vilma Baliukiene et al., 2001) and was effective to form crystalline Cu$_2$O and CuO. Also, this acts as a stabilizer for Cu (II) ions to prevent precipitation at high pH. Sodium hydroxide (NaOH) is used to adjust the pH of the solution. All the chemicals were Analar Grade Reagents. The electrolyte is prepared with 0.05M of Copper Sulphate Pentahydrate pure and 0.05M of tartaric acid. A solution of 1M of NaOH was prepared and was used to adjust the pH of the electrolyte. All solutions were prepared from doubly distilled water. Equal volume of copper sulphate solution and tartaric acid solution are added together and mixed well. This solution was used as the precursor for the deposition of thin films of Cu$_2$O and CuO.

3.4. Sample Preparation

3.4.1. Preparation Mechanism of Cu$_2$O

To prepare copper oxide thin films, a D.C. regulated power supply with three electrode system was used. The working electrode over which cuprous oxide has to be deposited is ITO coated glass plate. This acted as a cathode. The counter electrode was the platinum electrode and this was used as the anode for the cell. The reference electrode was Saturated Calomel electrode and was used to maintain the potential of the working electrode. Both the working and counter electrodes were kept closer and surfaces were kept parallel, so that the released ions were attracted and deposited exactly perpendicular to the cathode surface. The reference electrode tip was placed very close to the cathode surface so that the exact potential at the surface will be monitored unaffected by the solution resistance (internal resistance of the cell). When the cathode and the anode are connected across the power supply, the positive ions from electrolyte solution are attracted to the cathode, discharged and chemically reacted to form the material layer. Thus the potential between the working electrode
and the reference drives the electrochemical reaction at the working electrode’s surface. The current produced by the electrochemical reaction at the working electrode is balanced by the current flowing in the opposite direction at the counter electrode. The electrolyte was prepared by taking equal volume of 0.05M of Copper Sulphate Pentahydrate and 0.05M of tartaric acid. A solution of 1M of NaOH was prepared and was used to adjust the pH of the solution. Growth mechanism of Cu$_2$O films electrodeposited in ITO coated glass plate is as follows:

\[ \text{CuSO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} \quad (1) \]
\[ \text{Cu}^{2+} \cdot \text{T} \rightarrow \text{T}^* + \text{n}^- + \text{Cu}^{2+} \quad (2) \]
\[ 2\text{Cu}^{2+} + 2\text{e}^- + 2\text{OH}^- \rightarrow \text{Cu}_2\text{O} + \text{H}_2\text{O} \quad (3) \]

where, T is tartrate ion, T* oxidized tartrate ion, and Cu$^{2+}$-T represents a Cu(II)-tartrate complex. The first step of the reaction in the electrodeposition was the formation of Cu$^{2+}$ ions at the electrode surface due to cathodic reduction. Cu$^{2+}$ reacted with tartaric acid and formed copper tartrate complex. The second step was the formation of Cu$_2$O by reacting Cu$^{2+}$ with OH$^-$ (Poizot Philippe, 2003). From the above equation it is clear that the reaction depends on the OH concentration of the bath i.e. the pH of the bath.

At low pH values, presence of excess Cu$^+$ ions may favour the formation of Cu rich or Oxygen vacancies Cu$_2$O film. Therefore the high density of donors can be expected and the film may be n-type. When pH is high Cu$_2$O film prepared is with Cu vacancies. In other words, acceptor density will become significant and then the films become p-type. Thus films with more Cu vacancies form p type Cu$_2$O. Also it is clear that the OH$^-$ concentration value (pH) does not independently determine the
conduction type but it should also depend on the concentration of the Cu+ as well. At lower concentrations of Cu ions resulted in p-type films and higher concentrations resulted in n-type films at a pH value. At very low concentrations of Cu ions in the bath the tendency will be the formation of Cu vacancies in the films producing the p-type conductivity, irrespective of the pH. It is clear from the above results that the concentration of cupric ions and pH of the bath must be able to optimize to determine the values at which the n to p type transition occurs (Jayathileke, 2008).

3.4.1.1. pH Variation

The conduction type of the electrodeposited Cu$_2$O can be controlled by pH of the bath (Wang and Tao, 2007 and Jayathileke, 2008). The electrolyte was prepared by varying the pH and prior to the deposition, to study the deposition mechanism and the parameters needed for the deposition of cuprous oxide, electrochemical analysis was made by taking cyclic voltammetric curve. Electrochemical work station CHI-650C (CH Instruments, USA) was employed for electrochemical and electro analysis studies. The appropriate potential region in which the formation of stoichiometric Cu$_2$O and CuO thin films occurs was found to be between -800 mV and +600 mV. The scan rate was fixed as 0.05V/s and a scan segment of 2 was applied. Initially, in set I, five samples of cuprous oxide thin films were deposited on ITO coated glass plate by varying the pH of the electrolyte as pH9, pH10, pH11, pH12 and pH13 and these samples were coded as CU2O11, CU2O12, CU2O13, CU2O14, and CU2O15 respectively. Throughout the deposition process the temperature of the electrolyte was maintained at temperature 60°C. A cathodic potential of -0.05V was given to the working electrode. The deposition was done for a period of 60 minutes and the
deposition time was fixed after having tried many a time. After deposition the prepared samples were washed with doubly distilled water and air dried.

3.4.1.2. Temperature Variation

To analyse the effect of temperature of the electrolyte during the film formation, the temperature of the electrolyte is varied. The precursor was prepared with equal volume of 0.05M of CuSO₄ and 0.05 M of tartaric acid. 1M of NaOH was used to adjust the bath pH. The bath pH of the electrolyte was made as 12 and five samples were prepared by varying the temperature of the electrolyte at 40°C, 50°C, 60°C, 70°C and 80°C. The samples, set-II, were named as CU2O21, CU2O22, CU2O23, CU2O24, and CU2O25. Throughout the deposition process the temperature of the electrolyte was maintained at temperature 60°C. A cathodic potential of -0.50V was given to the working electrode. The deposition was done for a period of 60 minutes. After deposition the samples were washed with doubly distilled water and air dried. In total five samples were prepared to study the effect of temperature of the electrolyte.

3.4.1.3. Potential Variation

To study the effect of deposition potential applied on the working electrode, five samples were prepared. The precursor was prepared with equal volume of 0.05M of CuSO₄ and 0.05 M of tartaric acid. The bath pH was adjusted to pH12 using 1M NaOH. The potential given to the working electrode was varied as -0.40V, -0.45V, -0.50V, -0.58V and -0.63V. All potentials are reported with reference to the SCE scale. In set III five samples were prepared and are coded as CU2O31, CU2O32, CU2O33, CU2O34, and CU2O35. The deposition was done for a period of 60
minutes. After deposition the samples were washed with doubly distilled water and air dried.

Thus totally 15 samples of Cuprous oxide thin films were developed on ITO coated glass plate.

3.4.2. Preparation of CuO

Earlier studies on CuO deposition show that CuO formation occurs due to local pH decrease near the electrode surface or oxidation of Cu (II) to a meta stable Cu (III) species followed by chemical decomposition of the oxidized species. From Matijevic’s research (Sapieszko, R.S et al., 1980) on the synthesis of oxides by thermal decomposition of metal chelates, CuO precipitation is possible by electrochemical destruction of the soluble copper complexes. Due to its OH group, tartaric acid is a reducing agent, and can be oxidised irreversibly to various products. Cupric oxide deposition by electrochemical generation of acid is possible by the thermodynamic feasibility of oxidised water for E.=0.205V/SCE at high pH.

Growth mechanism of CuO films in electrodeposition is as follows:

\[
\text{CuSO}_4 \rightarrow \text{Cu}^{2+} + \text{SO}_4^{2-} \quad (1)
\]

\[
\text{Cu}^{2+}\cdot \text{T} \rightarrow \text{T}^* + \text{ne}^- + \text{Cu}^{2+} \quad (2)
\]

\[
\text{Cu}_{\text{aq}}^{2+} + 2 \text{OH}^- \rightarrow \text{Cu(OH)}_2 \rightarrow \text{CuO} + \text{H}_2\text{O} \quad (3)
\]

where T is tartrate ion, T* oxidized tartrate ion, and Cu\(^{2+}\).T represents a Cu(II)-tartrate complex. CuO is formed when anodic potential is given to the substrate. And, when the potential is positive tartaric ions are oxidised and Cu\(^{2+}\).T is broken. This produces precipitation of Cu\(^{2+}\) ions and copper hydroxide is a meta stable species and form
CuO at bath pH (Poizot Philippe et al., 2003). Throughout the deposition the bath temperature is fixed at 60°C and the films were coated for a period of 60 minutes.

### 3.4.2.1. pH Variation

The precursor was prepared with equal volume of 0.05M of CuSO$_4$ and 0.05 M of tartaric acid. The pH of the electrolyte was adjusted using 1M NaOH. When CuO was prepared by anodic potential and the deposition was done for a period of one hour the crystallinity was very poor. Also, the formation of CuO by anodic deposition requires a longer time. Therefore, the samples of Cu$_2$O were annealed to develop a better CuO crystal. A total of five samples were prepared by varying the pH of the electrolyte as pH 9, pH10, pH11, pH12 and pH13. Each sample was connected to the cell and cathodic potential of-0.50V was given to the working electrode and Cu$_2$O layers were deposited on the working electrode. The deposition was done for a period of 60 minutes. After deposition the samples were washed with doubly distilled water and air dried. These samples were then annealed to 500°C in muffle furnace for a period of 40 minutes. The annealed samples appear black from dark red which indicates the conversion of Cu$_2$O to CuO. The annealing temperature was fixed as 500°C by making many trials. When the samples were annealed from 100°C to 450°C there was traces of Cu$_2$O in the XRD report and when annealed above 500°C the CuO film gets peeled off. Therefore for the present work the annealing temperature was fixed at 500°C to get a better crystallization. CuO obtained by oxidation of cuprous oxide at higher temperature is represented by the equation

$$\text{Cu}_2\text{O} + \frac{1}{2}\text{O}_2 \rightarrow 2\text{CuO}.$$
The samples prepared were coded as CUO41, CUO42, CUO43, CUO44 and CUO45 in set IV. The samples were kept ready for analysis.

### 3.4.2.2. Temperature Variation

To study the effect of bath temperature, the precursor was prepared with equal volume of 0.05M of CuSO$_4$ and 0.05 M of tartaric acid. The pH of the electrolyte was adjusted using 1M NaOH. The bath pH was maintained at pH12. Each sample was connected to the cell and cathodic potential of -0.50V was given to the working electrode and Cu$_2$O layers were deposited on the working electrode. The deposition was done for a period of 60 minutes. The bath temperature was varied as 40°C, 50°C, 60°C and 70°C. After deposition the samples were washed with doubly distilled water and air dried. These samples were then annealed to 500°C in muffle furnace for a period of 40 minutes. Four samples were developed for temperature analysis and these samples were coded as CUO51, CUO52, CUO53 and CUO54. The samples were kept ready for analysis.

In total 9 samples of CuO were coated on ITO coated glass plates for further analysis.

### 3.4.3. Preparation of Heterojunctions

Of the wide variety of possible combinations for heterojunctions, CuO based solar cells have been prepared in the present work. Two hetero-junctions were prepared one with Cu$_2$O and other with n-type ZnO.

#### 3.4.3.1. ITO/CuO/Cu$_2$O Heterojunction

For the preparation of ITO/CuO/Cu$_2$O heterojunctions layer, the electrolyte was prepared with 0.05M of Copper Sulphate Pentahydrate pure and 0.05M of tartaric
acid. A solution of 1M of NaOH was prepared and was used to adjust the pH of the electrolyte. Equal volume of copper sulphate solution and tartaric acid solution were well mixed and the pH of the solution was maintained at 12. A potential of -0.50V was maintained for the deposition of cuprous oxide. By giving cathodic potential, Cu$_2$O was deposited on the substrate. The deposition was carried out for a period of 1 hr. After deposition the samples were washed with doubly distilled water and air dried. These samples were then annealed to 500°C in muffle furnace for a period of 40 minutes. The Cu$_2$O formed was converted into CuO. This substrate with ITO/CuO was then used as the working electrode and kept in the same electrolyte cell for further formation of Cu$_2$O. For the deposition of cuprous oxide a potential of -0.50V was given to the working electrode and the deposition was done for a period of 60 minutes. The film formed now is ITO/CuO/Cu$_2$O.

3.4.3.2. ITO/CuO/ZnO Film Heterojunction

CuO is prepared on ITO coated glass plate as mentioned in this chapter, 3.4.2. ZnO nano particles are deposited on ITO/CuO by SILAR method. SILAR is a modification of the chemical bath deposition technique and is also called ‘multiple dip coating’. 50 ml of 0.01M zinc sulphate was prepared and 0.05M of NaOH solution was added slowly to the above solution until the pH of the solution reaches pH10 and during this process the solution was stirred constantly by a magnetic stirrer. The solution was heated to 70°C and was maintained at the same temperature and is named as solution A. solution B contained doubly distilled water and was maintained at room temperature. The prepared ITO/CuO sample was then dipped in solution A for 10 sec and immediately in solution B for 10 sec. The process of dipping the
sample in solution A and B was repeated for 20 times and was known as 20 cycles. The reaction mechanism is as follows (Chandramohan et al., 2013):

\[ \text{ZnSO}_4 + 2\text{NaOH} \rightarrow \text{Na}_2 \text{ZnO}_2 + \text{H}_2\text{SO}_4 \]

\[ \text{Na}_2 \text{ZnO}_2 + \text{H}_2\text{O} \rightarrow \text{ZnO} + 2 \text{NaOH} \]

The prepared samples are washed and dried. Two heterojunction layers are prepared for application purpose.

All the prepared samples were characterized and are discussed in the successive chapters.
References


