Chapter 2
Materials and Methods

2.1. Copper Oxide

Syntheses of inorganic nano structures, with reliable low cost and well defined morphology have attracted attentions for the structural, optical and electrical characterization and their applications in various fields. Among different metal oxide materials, Cu based materials are of great interest because of their applications.

Copper oxide was the first substance known to behave as a semiconductor (http://www.ehow.com/how-12049723-CuO-Cu2O.html) and the study started in 1920’s and 30’s. But the interest in Cu$_2$O was revived after 1970’s. Copper oxide is a binary compound and it has two stable forms, Cuprous Oxide (Cu$_2$O) and Cupric Oxide (CuO). The physical properties, colours, crystal structures and electrical properties are different for Cu$_2$O and CuO. There are many reasons for selecting Cu$_2$O and CuO as the absorber layers for solar cell. They have better photoconductive and photochemical properties (Song et al., 2004, Li et al., 2005, Poizotetal., 2000, Liu et al., 2006, Rakhshni, 1986, Huand etal., 2002). In general they are non-toxic and their source material is abundant on earth. They have low band gap values and can be easily adjusted by altering the composition. They have high absorption coefficient in the visible range and can be prepared at low cost and in a simple method. They can be used in solar cells (Pankove et al., 1971), magnetic devices (Serin et al., 2005), and also they have radiation properties similar to those of an ideal black body (Serin et al., 2005). The two stable forms of copper oxides are discussed as follows.
2.2. Crystal structure, Properties and Application of Copper Oxide

2.2.1. Cuprous Oxide (Cu₂O)

Crystal Structure

Cuprous oxide is otherwise called copper (I) oxide or dicopper oxide or cuprite or red copper oxide. Copper oxide is found as the mineral cuprite in some red-colored rocks. It is red or yellow in colour depending on the size. It is an inorganic compound and is an attractive material for photovoltaic applications. It has a simple cubic crystal structure belongs to space group \( \text{Pn}\overline{3}m \) which includes the point group with full octahedral symmetry. Its lattice constant is 4.2696 Å. This structure is composed of two cubic sub-lattices: A face centered cubic lattice for the copper atoms and a body centered cubic lattice for the oxygen atoms. One sub-lattice is shifted by a quarter of the body diagonal in comparison with the other sub-lattice. The oxygen atoms are at the corners with a tetrahedral unit of \( \text{Cu}_4\text{O} \) at the centre. In the lattice each Cu atom coordinates with two \( \text{O}_2 \) atoms and each \( \text{O}_2 \) atom is surrounded by four Cu atoms, the unit cell contains 4 Cu atoms and 2 O atoms. The stoichiometry is 2:1 (Xue et al., 1990). Figure 2.1(a), (b) show the colour and the crystal structure of \( \text{Cu}_2\text{O} \) respectively.

![Fig. 2.1. (a)Cu₂O Color, (b) Crystal Structure of Cu₂O](image-url)
Properties of Cu₂O

Cu₂O is naturally a p-type material due to negatively charged Cu vacancies and has a direct band gap with values from 1.9 eV to 2.6 eV (Kari Brown et al., 2006). It is a non-toxic source material which is abundantly present on earth (Georgieva et al., 2003), and has high absorption coefficient in the visible range and a high optical transmittance at wavelengths above 600 nm. It has a large excitation binding energy of approximately 140 meV (Balamurugan et al., 2002, Olsen et al., 1979). Its melting point is 1235°C and boiling point is 1800°C. The density is 6 g/cm³ and the molar mass is 143.09 g/mass. The thermal expansion coefficient of Cu₂O is $3.5 \times 10^{-6}$°C. Its minority carrier lifetime $\tau$ is $10^{-8}$-$10^{-9}$ s at $T = 300$ K. The mobility of Cu₂O is $\mu = 70$ cm² V⁻¹ s⁻¹ at $T = 298$ K in oxygen saturated sample. It shows that it has diamagnetic property. It is insoluble in water and organic solvents. It tends to slowly oxidize to copper (II) oxide in moist air. Although it does not dissolve in water or any organic solvents, it reacts with strong acids such as hydrochloric, nitric, and sulphuric acids to form salts. Copper (I) oxide dissolves in concentrated ammonia solution to form the colourless complex $[\text{Cu(NH}_3)_2]^+$, which easily oxidizes in air to the blue $[\text{Cu(NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$. It dissolves in hydrochloric acid to form HCuCl₂ (a complex of CuCl), while dilute sulphuric acid and nitric acid produce copper (II) sulphate and copper (II) nitrate respectively.

The resistivity (lowest bulk resistivity) is 42 $\Omega$ cm at $T = 300$ K for sputtered film (Parreta et al., 1996), thermal activation energy of the conductivity $E_a$ is from 0.20-0.38 eV at $T = 298$ K for oxygen saturated sample, from 0.48-0.70 eV at $T=298 K$ for sample annealed at 1050°C and 0.49-0.70 eV at $T = 298$ K for sample
annealed at 750°C (Wang et al., 1982), 0.01 eV at T < 200 K and 0.18 eV at T > 200K for sputtered film (Parreta et al., 1996).

**Applications of Cu₂O**

This compound was one of the first semiconductors to be discovered. It also demonstrates the photoelectric effect, where exposure to light causes an electric current to flow. For this reason, it is used in photoelectric cells and light (Oba et al., 2005). One of the biggest uses of copper (I) oxide is found in agriculture. It is an ingredient in many fungicides used to protect a wide variety of crop plants from fungal diseases. Also, it is used as a pigment, and antifouling agent for marine plants. It is used in agricultural fungicide seed dressing. It provides sufficient copper for animals as mineral supplements in their diet, colorant for porcelain, glazes and glass. It also serves as catalysts in various dyes and pharmaceutical industries. A ceramic material made of it acts as a superconductor at relatively high temperatures. Superconductors that do not require extreme cooling to operate are still an area of active research. The compound is also the active component in many antifouling paints, which are used to protect ships and undersea structures preventing against encrusted with marine plants and animals.

Single crystal cuprous oxide can be prepared by different methods like thermal oxidation of Cu, sputtering, floating zone method and from melt. Polycrystalline cuprous oxide can be synthesized by anodic oxidation, sputtering, spray pyrolysis, pulsed laser deposition, molecular beam epitaxy and electrochemical deposition.

Electrochemical deposition method is more advantageous than any other method. This can be done at low temperature less than 100°C and the film quality can
be controlled. Also, different kinds of Cu₂O based solar cells have been fabricated with metal/p-Cu₂O Schottky junctions, p-n hetero and p-n homo junctions.

2.2.2. Cupric Oxide (CuO)

Crystal Structure

Cupric oxide or CuO is also called black copper or Copper (II) oxide or tenorite and is named after Prof. Michela Tenore, an Italian botanist at the University of Naples, Italy. It is a secondary copper mineral, a rare earth metal, and the most stable form of oxidised copper and is found in the oxidised zone of hydrothermal copper deposits, a volcanic sublimate. Cupric oxide belongs to the monoclinic crystal system, with a crystallographic point group of 2/m or C2h. The space group of its unit cell is C2/c. ("tenorite Mineral Data", htt://web mineral. Com /data/ tenorite.shtml). The native Cu vacancies in CuO makes it a p-type semiconductor and the band gap value is narrow (Song et al., 2004 and Li et al., 2005). Each atom in CuO has four nearest neighbours. In (110) plane each Cu atom is linked to four nearly co-planar oxygen atoms at the corner of the parallelogram. The oxygen atom is coordinated to four Cu atoms in the form of a distorted tetrahedron. The lattice constants are a= 4.6837 Å, b= 3.4226 Å, c=5.1288 Å. The interfacial angles are α = γ = 90°and β=99.54° (Madelung et al., 1996).

Properties of CuO

Pure cupric oxide is a black solid with the density of 6.4 g/cm³. It also has a high melting point of 1330 °C and is insoluble in water. As in cuprous oxide, native copper vacancy in CuO makes it a p-type semiconductor. Different from cuprous oxide, cupric oxide has an indirect band-gap of 1.2 eV to 1.9 eV (Kari Brown et al., 2006). Mishina et al., 2001 reported n-type behaviour of CuO. They have large value
of solar absorbance and a partial transparency in the visible range. Its melting point is 1064ºC and has a hole mobility of $0.1-10 \text{ cm}^2/\text{Volts}$. The dielectric constant of CuO is 18.1 (Medelung, 2004). It shows paramagnetic property and the susceptibility is equal to $3.1 \times 10^{-7}$ mass unit at 17ºC. The refractive index has a value of 2.65498. Figs. 2.2(a) and (b) show the colour and the crystal structure of CuO.

![Fig. 2.2(a) Color of CuO](image1)

![2.2(b) Crystal Structure of CuO](image2)

**Applications of CuO**

CuO has been studied for its use in PEC cells and as a cathode in dye sensitized solar cells. CuO has a wide usage in making fibres, ceramics, gas analyses and for welding fluxes. Cupric oxide is used as a pigment in ceramics to produce blue, red, and green and sometimes grey, pink, or black glazes. It is also used to produce cuprammonium hydroxide solutions, and used to make rayon. It is also occasionally used as a dietary supplement in animals, against copper deficiency. Copper (II) oxide has application as a p-type semiconductor, because it has a narrow band gap of 1.2eV. It is an abrasive used to polish optical equipment. Cupric oxide can be used to produce dry cell batteries. It has also been used in wet cell batteries as cathode, with
lithium as anode, and dioxalane mixed with lithium perchlorate as electrolyte. Copper (II) oxide can be used to produce other copper salts. It is also used while welding with copper alloys (Behera et al., 2012). Also it is used as a high capacity electrode material for Li ion batteries (Chandrasekaran et al., 2013) and in electronic devices and is also an effective catalyst (Zhou et al., 2006) leading to the complete combustion of organic compounds field emission devices. It is also used as catalysts and sensors. CuO is used in solar energy transformation (Balamurugan et al., 2002). It is used as flux in copper and bronze metallurgy, in galvanic electrodes. It serves as solvents for chronic iron ores. It is used to manufacture wood preservatives (http://www.ehow.com/how-12049723-CuO-Cu₂O.html222 mzojetoo>). CuO nanoparticles are used in gas sensors (Li et al., 2004) and acting as an antimicrobial agent and also an antioxidant.

The syntheses of CuO have drawn much scientific attention due to their interesting size-dependent on chemical and physical properties and also the potential technological applications. It is an abrasive used to polish optical equipment. Copper (II) oxide can be used to produce other copper salts. It is also used when welding with copper alloys. Another use for cupric oxide is as a substitute for iron oxide in thermite. This can turn the thermite from an incendiary to a low explosive. These advantages make CuO as a suitable compound for new studies to determine its applicability as a material of solar cell, in particular due to its photoconductivity and photoelectric cell properties.

2.3. Work done on Cuprous, Cupric Oxides and Solar cells using Cu₂O and CuO.

There is a growing demand for energy sources and solar energy is one of the most sustainable energy resources for future energy supplies. To make the solar
radiation energy into electricity, copper oxide is a better material. A detailed survey of
the previous work done on cuprous, cupric oxide thin films and the preparation of
heterojunctions using Cu$_2$O or and CuO are discussed below.

Transparent conducting metal oxides, being n-type were used to produce
heterojunction cells using p-type Cu$_2$O. Pollack and Trivich, 1975, prepared first
photovoltaic cell using copper and copper oxide. They obtained the open circuit
voltage and short circuit resistance as 0.4V and 2mA/cm$^2$ respectively. Noguet et al.,
1977, produced Cu$_2$O using electrodeposition. He adopted cathodic reduction of an
alkaline cupric lactate solution on transparent conducting glass slides. Trivich and
Economou, 1982, produced good quality polycrystalline Cu$_2$O by thermal oxidation
with resistivity in the range of 100-10000 ohm cm. The resistivity of Cu$_2$O film as
low as 25 ohm cm has been produced by Drobny et al., 1979, by reactive sputtering
technique. Olsen et al., 1979, reported Cu$_2$O with resistivity less than 100 ohm cm.
Herion et al., 1980, and Georgieva and Ristov, 2003, used ITO plates to coat Cu$_2$O
and in all the cases the resistivity was found to be high and efficiency low.

Papadimitriou et al., 1981, studied ZnO/Cu$_2$O junction solar cell and they
obtained the best values of open circuit voltage (Voc) in the order of 0.3V. Diwakar et
al., 2006, prepared CuO nanoparticles on SnO$_2$: F over layer by dip coating at room
temperature and the films sintered at around 400-500°C that gives higher photo
current. The band gap was found to be 1.72-1.79 eV by UV-Vis spectrophotometer.
They also observed that the resistivity increases with thickness. Economou et al.,
1982, produced Cu$_2$O thin film by electrodeposition and found that the resistivity is
very high in the order of $10^4$ to $10^6$ ohm cm. Olsen et al., 1979, studied the photo
response of Cu$_2$O. Sears et al., 1984, observed that excess of oxygen gives p-doped
semiconductor. Sears and Fortin, 1984, synthesized cuprous oxide films on copper substrates to a thickness of a few micrometres, using both thermal and anodic oxidation techniques. They found that the photovoltaic properties of the resulting Cu$_2$O/Cu back wall cells depend critically on the copper surface preparation, as well as on the specific conditions of oxidation. Back wall cells of the thermal variety with thickness down to 3 μm do not quite yet approach the performance of the best Cu$_2$O front cells, but are much simpler to grow. Serious difficulties with shorting paths in the case of thermally grown oxide and with the purity of the Cu$_2$O in the anodic case will have to be solved before a solar cell with an oxide layer thickness in the 1.5 to 2 μm range can be produced. Iwanoski, 1985, obtained Cu$_2$O by using Cu surface and deposited Cu$_2$O by hydrogen ion bombardment.

Rakshani et al., 1986, prepared Cuprous oxide by electrodeposition. They reported that cuprous oxide film was electrodeposited at different bath pH values showed two preferred orientation (100) and (111). Rakshani et al., 1987, cathodically electrodeposited Cu (I) oxide film onto conductive substrates from a solution of cupric sulphate, sodium hydroxide and lactic acid. Films of Cu$_2$O were deposited in three different modes, namely the potentiostatic mode, the mode with constant WE potential with respect to the CE and the galvanostatic mode. The composition of the films deposited under all conditions was Cu$_2$O with no traces of CuO. The optical band gap for electrodeposited Cu$_2$O films was 1.95 eV. The deposition temperature played an important role in the size of deposited grains. The films were photoconductive with high dark resistivity. Rakshani and Varghese, 1987, electrodeposited cuprous oxide thin films galvanostatically on 0.05 mm thick stainless steel substrates at a temperature of 600°C. The deposition solution with pH9 consisted
of lactic acid (2.7 M), anhydrous cupric sulphate (0.4 M), and sodium hydroxide (4 M). They found that all the films deposited at 60°C consisted only of Cu$_2$O grains a few μm in size and preferentially oriented along (100) planes parallel to the substrate surface. A band gap was found and it was 1.90-1.95 eV. Mukhopadhyay et al., 1992, electrodeposited Cu$_2$O on Cu substrate and studied the current voltage characteristics and electrical conductivity.

Sripala et al., 1996, prepared Cu$_2$O by electrodeposition and found that the film exhibits a direct band gap of 2.0 eV and reported n-type behaviour of cuprous oxide when used as a liquid /solid junction in a photo electrochemical cell. Golden et al., 1996, found that the reflectance and transmittance of the electro deposited films of cuprous oxide give a direct band gap of 2.1 eV. The authors used electrodeposition method for obtaining the films of cuprous oxide by reduction of copper (II) lactate in alkaline solution (0.4 M cupric sulfate and 3 M lactic acid). The films were deposited either on stainless steel or on indium tin oxide (ITO) substrates. The deposition temperatures ranged from 25 to 65°C. They found that the cathodic deposition current was limited by a Schottky-like barrier that forms between the Cu$_2$O and the deposition solution. A barrier height of 0.6 eV was determined from the exponential dependence of the deposition current on the solution temperature. At a solution pH9 the orientation of the film is [100], whereas at a solution pH12 the orientation changes to [111]. The degree of [111] texture for the films grown at pH12 increased with applied current density.

Musa et al., 1998, produced cuprous oxide by thermal oxidation and studied its physical and electrical properties. In this, Cu foils were heated in the range of 200 to 1050°C. It was observed that the single phase Cu$_2$O exists on the temperature range of
1040-1050°C and the mixture of Cu₂O and CuO was observed between 200 and 950°C. Zhou, Y.C et al., 1998, deposited polycrystalline Cu₂O films on stainless steel substrate by galvnostatic electrodeposition method and they observed that the films were deposited at low bath pH<7 consisted of Copper (I) oxide and metallic copper; while the films deposited at bath pH between 8 and 12 and bath temperature at 60°C were pure Copper (I) oxide. Nair et al., 1999, used aqueous solution of copper complex and NaOH and electrochemically deposited copper oxide thin film on glass substrate and studied its structural, optical and electrical characteristics. Jongh, P.E et al., 1999, electrodeposited Cu₂O on TFO conducting substrate. It was observed that the temperature of the deposition solution ranging from 10-60°C had a strong influence on the morphology of the oxide and the pH of the solution strongly influences the nucleation process.

Fernando et al., 2000, reported synthesis method of boiling copper plates in CuSO₄ or HCl solution to prepare Cu₂O film, and observed an n-type signal from a photo-electrochemical cell. Mahalingam et al., 2000, deposited cuprous oxide thin films on copper and tin oxideoated glass substrates by cathodic reduction of alkaline cupric lactate solution (0.45 M CuSO₄, 3.25M lactic acid and 0.1 M NaOH). The deposition was carried out in the temperature range of 60-800°C at pH9. Galvanostatic deposition on tin-oxide-coated glass and copper substrates yields reddish-grey Cu₂O films. All the films deposited are found to be polycrystalline having grains in the range of 0.01-0.04 μm. The deposition kinetics is found to be linear and independent of the deposition temperature. From the optical absorption measurements, authors found that the deposit of cuprous oxide films has a refractive index of 2.73, direct band of 1.99 eV, and extinction coefficient of 0.195. After deposition on temperature
of 700°C, cuprous oxide films were annealed in air for 30 minutes at different temperatures (150, 250 and 350°C) to obtain their room temperature resistivity. It showed a decrease in resistivity of Cu$_2$O film of the order of 10$^7$ Ωcm to 10$^4$ Ωcm. The explanation of such behaviour may be due to increase in the hole conduction.

Ghosh et al., 2000, deposited cuprous oxide and cupric oxide by RF reactive sputtering at different substrate temperatures, namely, at 30°C, 150°C and 300°C. From AFM image it was found by for the film deposited at 300°C, that, 8-10 small grains of size ~40nm diameter agglomerate together and make a big grain of size ~120 nm. The grain size becomes 160 nm at the temperature of 150°C. The grain size decreases to 90 nm at 300°C. From thickness and deposition time, the deposition rates of the films are found to be 8, 11.5 and 14.0 nm/min for substrate temperatures corresponding to 30°C, 150°C and 300°C, respectively. The optical band gap of the films deposited at 30°C, 150°C and 300°C are 1.75, 2.04 and 1.47 eV respectively. Different phases of copper oxides are found at different temperatures of deposition. The CuO phase is obtained in the films prepared at a substrate temperature of 300°C. Yoon et al., 2000, studied the photoelectro chemical properties of copper oxide thin films coated on an n-Si substrate. The n-silicon photoelectrode with CuO phase showed better photoelectron conversion efficiency than that of Cu$_2$O phase.

Balamurugan and Metha et al., 2001, prepared copper oxide thin film by activated reactive evaporation method and studied its structural and optical properties. The optical studies shows directly allowed transition. He showed that a single nanocrystal can be grown at low substrate temperature. Oguru et al., 2001, grew CuO and analysed the structural and electrical properties of CuO.
Borgohain et al., 2002, synthesized cuprous oxide quantum particles and studied its properties. They used two methods. One is conventional chemical route. This was done by heating copper tartrate complex with glucose in the presence of a capping agent i.e. polyvinyl pyrrolidone (PVP) and obtained cuprous oxide. In the other method cuprous oxide was synthesized using a modified electrochemical route. Copper and platinum electrodes were used as the anode and cathode respectively. The electrolyte bath contained acetonitrile and tetrahydrofuran in the ratio of 4:1. Tetra-n-octul ammonium bromide was also used as a stabilizer. Quantum dot sizes of 2 and 8 nm were obtained by applying a current density of 50 and 2mA/cm².

Valtierra et al., 2002, coated copper oxides on fibre glass, particularly in the form of 6CuO.Cu₂O with the help of chemical vapour deposition using the precursor (acac)₂ Cu(II). They observed that only cuprous oxide was formed at a temperature of 320°C and cupric oxide was formed at a higher temperature of about 340°C and at a temperature of 325°C, 6CuO.Cu₂O was formed.

Leopold et al., 2002, used Cu (II) tartrate to deposit cuprous oxide on Copper. Also he prepared the same using tartrate based solution. Fernando et al., 2002, reported n-type photo responses from Cu plates immersed in CuSO₄ solution for a few days. He also reported n-type Cu₂O by heating Cu sheets in CuSO₄ solution.

Amelao et al., 2003, synthesised nano plastic Copper oxide thin film by sol-gel method using copper acetate monohydrate precursor in ethanol as a solvent. They used silica slides as substrate. The films were deposited in air at room temperature by keeping a controlled withdrawal speed of 7 cm/sec. Coating were obtained by means of a multi-dipping process. Liu, R et al., 2003, electrodeposited epitaxial bulk Cu₂O film on InP with tunable morphologies. Potentiostatic deposition of Cu₂O nanowires
in polycarbonate membrane by cathodic reduction of alkaline cupric lactate solution was studied by Daltin, A.L et al., 2005, Poizot et al., 2003, developed CuO by electrochemical deposition with Cu (II) tartrate complex. He used alkaline medium and prepared CuO by anodic deposition and Cu₂O by cathodic deposition.

Lee et al., 2004, prepared cuprous oxide to use it as an anode material in thin film lithium batteries. Nakaoka et al., 2004, prepared cupric and cuprous oxide on platinum and gold substrate from Cu (II) solutions with various amino acids. They observed that both the copper oxide films prepared are found to be typical p-type semiconductors. Optical band-gap energies of CuO films depend on the amino acids used and the value of Eg for the Cu₂O film is 2.17 eV. Takeshi Fujiwara et al., 2004, fabricated Cu₂O on Ti substrate using tartaric acid as chelating agent and used Platinum plate as counter electrode. They observed that Cu₂O film shows (100) faceted grains with ~2μm in size. This morphology indicates their oriented growth along <111> axis, which is inconsistent with the XRD data where apparent (111) orientation can be seen.

Tang Yiwen et al., 2004, electrodeposited Cu₂O on TiO₂ film. He studied the effect of pH and temperature and found that pH between 5.5 and 6 are the best for Cu₂O. He also calculated the resistivity of Cu₂O and CuO and found that annealing decreases the resistivity. Tanaka et al., 2004 have prepared Cu₂O with TCOs. They used indium oxide and tin oxide and multicomponent oxides like aluminium-zinc-oxide (AZO) and aluminium-zinc-tin-oxide (AZITO) in addition to ZnO. Highest efficiency of 1.2% was obtained with AZO/Cu₂O devices prepared at 150°C.
Copper (II) oxide thin films were prepared by Oral et al., 2004, using sol-gel method on microscope film substrates using copper acetate in isopropyl alcohol and measure optical band gap between 1.6 eV -1.75 eV. Zhang et al., 2004 prepared ITO/ZnO/Cu$_2$O heterojunction and the structure offered an easy way for electrons form n type ITO to p-type Cu$_2$O and blocked the back hole injection from the p to n side when forward bias voltage is applied. Also ZnO made smoother energy band edge between Cu$_2$O and ITO and decreased the interfacial conduction and the valence band discontinuities and made easy transition between Cu$_2$O and ITO. Song et al., 2004, Li et al., 2005, Poizot, 2000, Tarascon and Arand, 2001, Rakshani, 1986.

Bannerjee and Chattopadhyay, 2005, found that CuO has high solar absorbency and low thermal emittance. Kotaro Mizuno et al., 2005, electrodeposited p-type Cu$_2$O films on a conductive substrate by electrodeposition at 318 K from an aqueous solution containing copper sulphate and lactic acid. The structural and electrical characterizations of the resulting films were studied. From Hall Effect measurement the resistivity was found to vary from $2.7 \times 10^4$ to $3.3 \times 10^6$ ohm cm. Liu et al., 2005 investigated the electrochemical deposition of Cu$_2$O films on three different substrates (indium tin oxide film coated glass, n-Si wafer with (001) orientation and Au film evaporated onto Si substrate). For the film grown on ITO, the electrical current increases gradually during deposition, while the films growing on both Si and Au substrates, the monitored current decreases monotonically. Authors considered that the continuous decrease in current reflects different deposition mechanisms. In the case of Si substrate, the decrease of the current may be the result of the formation of an amorphous SiO$_2$ layer on the Si surface, which limits the current. For the Au surface, the decrease in measured current is due to the resistivity
increase as a result of Cu$_2$O film formation. Cu$_2$O crystals with microsized pyramidal shape were grown on ITO substrate. Nanosized and pyramidal shaped Cu$_2$O particles were formed on Si substrate and the film grown on Au substrate shows a (100) orientation with much better crystallinity.

Tang et al., 2005, investigated the electrochemical deposition of nanocrystalline Cu$_2$O thin films on TiO$_2$ films coated on transparent conducting optically (TCO) glass substrates by cathodic reduction of cupric acetate (0.1 M sodium acetate and 0.02 M cupric acetate). Authors concluded that the pH and bath temperature strongly affect the composition and microstructure of the Cu$_2$O thin films. The effect of bath pH on electrodeposition of Cu$_2$O thin film was investigated by selecting a bath temperature of 300°C and an applied potential of -245mV vs SCE. Authors found that the films deposited at pH4 are mostly metallic Cu and there is only little Cu$_2$O. In the region of pH4 to pH5.5, the deposited films are a composite of Cu and Cu$_2$O, while the films deposited at pH between 5.5 and 6 are pure Cu$_2$O. Pure Cu$_2$O deposited at bath temperature between 0°C and 300°C produced spherically shaped grains with 40–50 nm in diameter. The bath temperature must be controlled in the range of 0-300°C to obtain nanocrystalline Cu$_2$O thin film. A highly branched dendrite formed at a temperature of 45°C, and the grain size was increased to 200–500 nm. A ring-shaped structure with a porous surface was observed at the temperature above 60°C. The optical absorption measurements indicate that annealing at 200°C can improve the transmittance of the nanocrystalline Cu$_2$O thin films. Ogwu et al., 2005, sputtered copper oxide films on glass plate by reactive RF magnetron sputtering using a solid copper target and an Argon-Oxygen gas atmosphere. He observed a maximum transmission between 40% and 80% and the optical band gap
values of the films ranged between 2.05 and 2.4 eV. Mahalingam et al., 2005, potentiostatically deposited Cu$_2$O thin films and carried out the structural and annealing studies. The obtained a single-phase cubic Cu$_2$O films in the deposition potential range from -0.355 to -0.555V vs SCE. When the deposition potential varied from -0.355 to -0.755Vs SCE in steps of 0.1, they found the grain sizes as 26, 31, 55, 25 and 20nm. They also observed that the optimum potential for Cu$_2$O is -0.555V vs SCE. Papadimitropoulos et al., 2005, synthesised copper oxide by oxidation of copper thin film on silicon substrate in temperature varying from 150°C to 450°C. Pure Cu$_2$O was obtained at 225°C and pure CuO was formed above 350°C. Nozik et al., 1978, and Tang et al., 2005, prepared Cu$_2$O for solar cells. Tang et al., 2005, found that the band gap of nanocrystalline Cu$_2$O thin films is 2.06 eV.

Mahalingam et al., 2006, developed Cu$_2$O thin film by cathodic reduction of copper II lactate solution at a potential of -0.555 V Vs SCE, at a bath pH9 and at a bath temperature 70°C. Wang, L., 2006, prepared Cu$_2$O with copper sulphate and lactic acid. The lactic acid was to stabilize Cu (II) ions at a bath pH higher than 7.0. He observed that the growth rate of the film depended on the deposition time at a constant temperature of 60°C and a constant pH of 9.0, 10.0 and 12.5. He also observed that if deposition time increased the growth rate would decrease because the effect on conductivity in the cell by indium tin oxide was replaced by a less conductive material i.e. Cu$_2$O. Also, he prepared both n and p type cuprous oxide thin films.

Wijesundera et al., 2006, investigated the potentiostatic electrodeposition of cuprous oxide and copper thin films. Electrodeposition was carried out in an aqueous solution containing sodium acetate and cupric acetate. The results of their
investigation show that the single phase polycrystalline Cu$_2$O can be deposited from 0 to -300 mV vs SCE. Also, the co-deposition of Cu and Cu$_2$O started at -400 mV vs SCE. At the deposition potential from -700 mV vs SCE a single phase Cu thin films were produced. Single phase polycrystalline Cu$_2$O thin films with cubic grains of 1–2 μm could be possible at the deposition potential around ~200 mV (SCE).

Template mediated electroplating was used to fabricate Cu$_2$O nano rod arrays by Lee, Y.H et al., 2006. Brown, K.E.R et al., 2006, synthesised a highly transparent Cu$_2$O film approximately with 10 nm sized nano rods. Akimoto et al., 2006, prepared Cu$_2$O on glass substrate by reacting magnetron splitting method. Diwakar et al., 2006, prepared CuO thin film for photo electro chemical splitting of water. He observed that the optical band gap varies from 1.72-1.79eV. The films prepared at low sintering temperature (400-500°C) yield higher photo current and are efficient for photo splitting of water. He also observed that the resistivity increases with thickness and observed that the thicker films are less effective in photo conversion.

Alberto Mittiga et al., 2006, prepared ITO/ZnO/Cu$_2$O heterojunction solar cell and reported 2% efficiency. Cu$_2$O thin films were deposited on a TiO$_2$ substrate typically form a p-n heterojunction. This system has been widely investigated for photocatalysis and solar cell applications films on Cu$_2$O substrates. Akimoto et al., 2006, Musa et al., 1998, Nozik et al., 1978, Tang et al., 2005, used Cu$_2$O in solar cells. Longcheng and Meng, 2007, electrochemically deposited Cu$_2$O by varying solution pH and produced p-n homojunction of Cu$_2$O.

Mattew J. Siegfried et al., 2007, prepared CuO by anodic deposition in acidic media of copper acetate (pH5.5-6.4). The band gap and flat band potential are estimated to be 1.37eV and 0.26V in a 0.1M Na$_2$HPO$_4$ solution with pH9.2.
Guo et al., 2007, electrodeposited Cu$_2$O microcrystals. A perfect Cu$_2$O octahedral and mono disperse colloid spheres were obtained. Wang et al., 2007, cathodically electrodeposited cuprous oxide films from 0.4 M copper sulphate bath containing 3 M lactic acid. The bath pH was carefully adjusted from 7.5 to 12.0 by controlled addition of 4 M NaOH. The electrodeposition was done on Sn-doped indium oxide substrates. The influence of electrodeposition bath pH on grain orientation and crystallite shape was examined. Authors found that three orientations, namely, (100), (110), and (111) dominate as the bath pH is increased from ~ 7.5 to ~ 12.

Singh et al., 2007, synthesized cuprous oxide nanostructures by anodic oxidation of copper through a simple electrolysis process employing plain water as an electrolyte. No special electrolytes, chemicals, and surfactants were used. Platinum was taken as cathode and copper as anode.

Singh et al., 2008, estimated the band gap of prepared Cu$_2$O nano threads and nanowires to be 2.61 and 2.69 eV, which is larger than the direct band gap (2.17 eV) of bulk Cu$_2$O (Wong and Searson, 1999). Sumy et al., 2008, deposited Cu$_2$O on stainless steel substrate at pH12 and obtained triangular pyramidal morphology and when pH > 14, crystallites are with octahedral morphology. If pH ≥ 12, a single phase Cu$_2$O coating oriented in the (111) direction was obtained. Also, he observed that Cu$_2$O is stable only in the potential range -0.30V to -0.50V and at high pH. Jeyathileke et al., 2008, prepared n-p and p-n homojunction cuprous oxide thin film in aqueous acetate bath. He observed that conductivity type of the film depends on pH and also the cupric ion concentration.
Jayatissa et al., 2009, prepared cuprous oxide (Cu$_2$O) and cupric oxide (CuO) thin films by thermal oxidation of copper films coated on indium tin oxide (ITO) glass and non-alkaline glass substrates. The formation of Cu$_2$O and CuO was controlled by varying oxidation conditions such as oxygen partial pressure, heat treatment temperature and oxidation time. The experimental results suggest that the thermal oxidation method can be employed to fabricate device with good quality Cu$_2$O and CuO films.

Hu et al., 2009, electrodeposited Cu$_2$O thin films on an indium tin oxide (ITO) coated glass by a two-electrode system with acid and alkaline electrolytes under different values of direct current densities. Copper foils were used as the anodes, and the current density between the anode and cathode varied between 1 mA cm$^{-2}$ and 5 mA cm$^{-2}$. It was obtained that the microstructure of Cu$_2$O thin films produced in the acid electrolyte changes from a ring shape to a cubic shape with the increase of direct current densities. The microstructure of Cu$_2$O thin films produced in the alkaline electrolyte has a typical pyramid shape. The electrocrystallization mechanisms were considered to be related to the nucleation rate, cluster growth, and crystal growth. Different current densities with the same deposition time were applied to investigate the initial stage of nucleation and cluster growth.

Mc Shane et al., 2009, observed obvious photocurrent enhancement of n-type Cu$_2$O films by controlling the dendritic branching electrochemical deposition growth.

Han and Tao, 2009, found that n-type Cu$_2$O deposited in a solution containing 0.01 M copper acetate and 0.1 M sodium acetate exhibits higher resistivity than p-type Cu$_2$O deposited at pH13 by two orders of magnitude. Kunhee and Meng, 2009,
also produced p-n homojunction Cu$_2$O solar cell. It has efficiency only of 0.1% due to high resistivity of p and n Cu$_2$O layers.

Aiping Chen et al., 2010, prepared Cu$_2$O and CuO on Si substrate by pulsed laser deposition and studied the structural and optical characteristics. Swarup Kumar et al., 2010, fabricated nano sized CuO film and found that the band gap is 3.1 eV and confirmed that the increases in band gap is due to quantum confinement effect resulting from decrease in the dimension of structure and the size. Mahalingam et al., 2010, prepared CuO on ITO by electrodeposition and studied the effect of deposition potential on the physical properties.

Wijesundera et al., in 2010, electrodeposited single-phasic Cu$_2$O on Ti/CuO electrodes in an aqueous solution containing 0.1 M sodium acetate and 0.01 M cupric acetate in the potential range of -250 to -550 mV/SCE. Well-covered photoactive n-type Cu$_2$O thin films were electrodeposited on the Ti/p-CuO electrode at -550 mV vs SCE in similar electrolytic conditions in which Cu$_2$O was deposited on the Ti substrate. It was concluded that the thicknesses of the CuO and Cu$_2$O semiconducting layers and annealing of the CuO/Cu$_2$O hetero-junction played a major role in enhancing the photoresponse in the PEC water splitting.

Wenyan et al., 2011, electrodeposited Cu$_2$O and studied its photoelectrochemical properties. He studied the variation of deposition potential with crystal growth and observed that when deposition potential is more negative the particle size decreases. Rajani, K. V et al., 2011, reported on the direct formation of Cu$_2$O by microwave plasma oxidation of pulsed dc magnetron sputtered Cu films. The grain size was found to be from 20 to 30 nm and the resistivity around 66 ohm cm. Also the optical absorption coefficient value is around $10^5$/cm for Cu$_2$O film.
Wijesundera, 2011, electrodeposited Cu$_2$O thin film for fabrication of CuO/Cu$_2$O heterojunction using an electrodeposition technique for solar cell applications and he observed that resistivity was high and of the order of $10^4$ to $10^6$ ohm-cm. Wilman et al., 2011, fabricated Cu$_2$O/Al-doped ZnO heterojunction solar cell on FTO coated glass plate. The highest efficiency of 0.6% was obtained with a Cu$_2$O film deposited at -0.6V vs Ag/AgCl. Also they obtained open circuit voltage of 0.29V, short circuit current density of 7.12% and a fill factor of 0.292. This was attributed to better compactness and purity of the Cu$_2$O film than those of the Cu$_2$O films deposited at other potentials. Wilman Septina et al., 2011, developed Cu$_2$O thin film and found that the grain size decreases as the potential increases and was due to frequencies of nucleation of Cu$_2$O crystals during deposition that tends to be higher when the applied potential becomes more negative. Mohd Rafie Johan, 2011, found that the band gap of CuO is in between 1.21eV and 1.51eV and Cu$_2$O, between 2.10 eV and 2.60 eV.

Ahmad Rahnama et al., 2012, prepared CuO nanoparticles via simple precipitation method at different reaction temperatures. They observed that the crystalline size and crystallisation increased with the increase in the temperature from 10 to 115°C. The band gap of the samples was calculated to be in the range of 1.9 eV to 2.9eV. Ezenwa, 2012, deposited CuO on glass substrate by chemical bath deposition using copper sulphate and EDTA. He found that the optical band gap was about 1.7eV. Also he obtained the absorption approximately of 0.87 at the wavelength range of 300-320 nm. Jundale, 2012, synthesized CuO by sol-gel using cupric acetate and methanol. They also calculated that the conductivity varies from $10^{-6}$ to $10^{-5}$ (ohm cm)$^{-1}$. Sadeghi, 2012, prepared copper oxide thin film by PVD on glass substrate at
90 nm thickness and post annealing at different temperature 200-400°C. The band gap varies from 1.8 eV to 2.56 eV.

Paula Grez et al., 2012, electrodeposited n-Cu$_2$O on fluorine-doped tin oxide pre-deposited glass substrates from aqueous solution of Cu (II) acetate. The potential applied was -0.450V vs SMSE at 70°C. They obtained high crystallinity cubic Cu$_2$O and a strong preferential growth along the (200) and (220) directions. Hiroki Kidowaki et al., 2012, fabricated CuO/ZnO and ZnO/CuO heterostructures on indium tin oxide by electrodeposition. They used copper sulphate and lactic acid and the pH of the solution was adjusted to 12.5 by NaOH. The solar cell with a CuO/ZnO structure provided power conversion efficiency ($\eta$) of 1.1×10$^{-4}$ %, fill factor (FF) of 0.25, short-circuit current density (Jsc) of 1.9 mAcm$^{-2}$ and open-circuit voltage (Voc) of 2.8 × 10$^{-4}$ V. The optical absorption of CuO is in the range of 400 to 700 nm and the crystal size was found to be 49 nm.

Zainelabdin et al., 2012, prepared CuO/ZnO nanocorals p-n heterojunction on ITO substrate at low temperature of 60°C. The contact resistance of Au and ITO to CuO and ZnO were found to be about 3.2 ×10$^{-3}$ ohm and 1.7×10$^{-3}$ ohm respectively.

Wei et al., 2012, fabricated p/n type Cu$_2$O films by electrochemical deposition using different electrolytes and optimising pH level. The growth rate of n-Cu$_2$O was tuned from (100) to (111) by decreasing the applied potential and the growth of p-Cu$_2$O was grown over the layer with the same (111) orientation that facilitated the formation of a homojunction with high quality interface.

Laxmi, J et al., 2013, studied the optical properties of hydrothermally synthesized Cu/Cu$_2$O/CuO nanocrystals. The average crystallite size of the sample
was found to be around 27 nm. The absorption spectra show two broad peaks situated at 354 nm and 466 nm respectively and each absorption peak corresponds to two different phases. The absorption in the visible region of the spectrum gave evidence of the presence of oxygen. The optical band gap was calculated by Tauc’s plot. Two different band gaps corresponding to two different phases, Cu$_2$O and CuO were evaluated for each sample.

Quang et al., 2013, prepared highly aligned Cu$_2$O/CuO/TiO$_2$ on Au substrate by air annealing of the electrodeposited Cu nanowires and with dip coating. Cetinkaya et al., 2013, fabricated CuO/p-Si Schottky diodes by CBD and sol-gel methods and studied its characterization. They observed that the film grown by CBD is denser than the film grown by sol-gel method and found that the average size of CuO particle is approximately equal to 15 nm.

Xishun Jiang et al., 2014, electrodeposited Cu$_2$O nanocrystalline thin film on Ti substrate using sodium acetate and cupric acetate for different potentials (-0.1, -0.3, -0.5, -0.7, and -0.9 V) and studied its optical properties. Electrodeposition was carried out under potentiostatic condition at different applied potentials (-0.1, -0.3, -0.5, -0.7, and -0.9 V) with respect to the reference electrode. The optical band gap value varies from 1.69 eV to 2.03 eV.

Chen et al., 2014, deposited Cu$_2$O thin film by chemical bath deposition and studied the influence of deposition temperature on growth process. They used copper sulphate as the copper precursor. The crystal size varies in the range of 33-51 nm and the band gap varies from 2.47 eV to 2.61 eV when the deposition temperature is in the range of 60-90°C. Also the UV-Vis absorption spectra show a blue shift.
According to the review of work done on the copper oxides, it is observed that different precursors were used to fabricate Cu$_2$O, yet only a very few reports are available for Cu$_2$O preparation using copper tartrate complex. Hence this present work is an attempt to prepare Cu$_2$O using copper tartrate complex and to convert into CuO and further to fabricate CuO based heterojunction under optimized condition.

2.4. Different Deposition Techniques

The properties of thin films are extremely sensitive to the method of preparation. The deposition techniques fall into two broad categories, depending on whether the process is primarily chemical or physical, it has been classified as physical vapour deposition and chemical vapour deposition.

1. Physical Deposition Techniques

In case of physical deposition methods, atoms are directly transported in a gas phase from the source material to be deposited onto the substrate forming a thin layer of solid. It uses mechanical, electromechanical or thermodynamic means to produce a thin film of solid. Different types of physical deposition are given below: i) Thermal evaporation, ii) Electron beam evaporation, iii) Molecular beam epitaxy, iv) Sputtering, v) Pulsed laser deposition, vi) Electro dynamic deposition.

i) Thermal evaporation

It uses an electric resistance header to melt the material and raises its vapour pressure to a useful range. This is done in a high vacuum, both to allow the vapour to reach the substrate without reacting with or scattering against other gas-phase atoms in the chamber and reduce the incorporation of impurities from the residual gas in the
vacuum chamber. Obviously only materials with a much higher vapour pressure then the heating element can be deposited without contamination of the thin film.

ii) Electron Beam Evaporation

An electron beam evaporator fires a high energy beam from an electron gun to boil a small spot of material; since the heating is not uniform, lower vapour pressure materials can be deposited. The beam is usually bent through an angle of 270° in order to ensure that the gun filaments not directly exposed to the evaporate flux. Typical deposition rates for electron beam evaporation range from 1 to 10 nm/sec.

iii) Molecular Beam Epitaxy

In molecular beam epitaxy slow streams of an element can be directed at the substrate, so that material deposits one atomic layer at a time. Compounds such as GaAs are usually deposited by repeatedly applying a layer of one element (i.e. Ga) then a layer of other (i.e. As), so that the process is chemical, as well as physical. The beam of material can be generated by either physical means (i.e. by a furnace) or by a chemical reaction (chemical beam epitaxy).

iv) Sputtering

The ejection of atoms from the surface of a target by bombardment with energetic particles is called sputtering. During this process, a substrate is out of the chamber, and the target material is released into the chamber in the form of a gas. Strong magnets create a charge that causes the target during this process ensures that the thin film is evenly distributed on its surface. The thin film process creates the
films of various elements or molecules that range between a few and few hundred atoms thick.

v) Pulsed Laser Deposition

This systems work by an ablation process. Pulses of focused laser light vaporize the surface of the target material and convert it to plasma; this plasma usually reverts to a gas before it reaches the substrate.

vi) Electro Dynamic Deposition (Electro Spray Deposition)

It is a relatively new process of thin film deposition. The liquid to be deposited, either in the form of nano particle solution or simply a solution is fed to a small capillary nozzle (usually metallic) which is connected to a high power source. The substrate on which the film has to be deposited is connected to the ground terminal of the power source through the influence of electric field, the liquid coming out of the nozzle takes a conical shape (Taylor cone) and at the apex of the cone a thin jet emanates which disintegrates into very fine and small positively charged droplets under the influence of Rayleigh charge limit. The droplets keep getting smaller and smaller and ultimately get deposited on the substrate as a uniform thin layer.

2. Chemical Deposition

Chemicals either in liquid or gas forms, it can be used to create a thin film. Here, a fluid precursor undergoes a chemical change at solid surface, leaving a solid layer. Thin films from chemical deposition techniques tend to be conformal, rather than directional.

Chemical deposition is further categorized by the phase of the precursor as i)Chemical solution deposition or Chemical bath deposition(CBD), ii) Spin coating,

**i) Chemical Solution Deposition or Chemical Bath Deposition (CBD)**

It uses a liquid precursor, usually a solution of organo metallic powders dissolved in an organic solvent. This technique is also known as sol-gel method because the ‘sol’ (or solution) gradually evolves towards the formation of a gel-like diphasic system. The chemical bath deposition involves two steps, nucleation and particle growth, and is based on the formation of a solid phase from a solution. In the chemical bath deposition procedure, the substrate is immersed in an aqueous solution containing the precursors. It requires only solution containers and substrate mounting devices. It yields stable, adherent, uniform and hard films with good reproducibility by a relatively simple process.

**ii) Spin Coating**

It is a method to produce thin films using solutions, suspensions or liquid precursors (chemical preliminary stage). Preferentially it is applied for expensive or minor amounts of source solution. A solution is applied on a fast rotating substrate and nearly completely removed by spinning, so that only a thin film remains. Additionally, the majority of the eliminated solution can be collected and led back. Depending on the desired properties of the film the viscosity, the wetting behaviour and, if necessary, the solids content will be modified. Repeated depositions can be carried out to increase the thickness of the films as desired. Thermal treatment is often carried out in order to crystallize the amorphous spin coated film. Such crystalline
films can exhibit certain preferred orientations after crystallization on single crystal substrate.

iii) Chemical Vapor Deposition (CVD)

In this process, the substrate is placed inside a reactor to which a number of gases are supplied. The fundamental principle of the process is that a chemical reaction takes place between the source gases. The product of that reaction is a solid material which condenses on all surfaces inside the reactor.

iv) Plasma Enhanced Chemical Vapor Deposition (PECVD)

Thin films can be deposited on substrate surfaces by plasma enhanced decomposition of gaseous precursors. This process is characterized by low temperatures as compared to classical thermal CVD processes. In this way not only deposition of crystalline thin films is possible, but also amorphous Si films can be created. Liquid precursors can be used by vaporization of liquids in the so called bubbler.

v) Atomic Layer Deposition (ALD)

It uses gaseous precursor to deposit conformal thin films one layer at a time. The process is split up into two half reactions, run in sequence and repeated for each layer in order to ensure total layer saturation before beginning the next layer. Therefore one reactant is deposited first, and then the second reactant is deposited during which a chemical reaction occurs on the substrate, forming the desired composition. As a result of the stepwise, the process is slower than CVD. However it can be run at low temperatures, unlike CVD.
vi) Photo Chemical Deposition (PCD)

Photochemical deposition method involves direct irradiation of precursor bath with ultraviolet light. In PCD, the energy is absorbed by the precursor species. The absorbed photon may promote electrons to excited states. If UV or visible radiation is used, the ground state energy is increased by single or multi-photon absorption process at longer wavelengths. The PCD technique is simple, cheap, having better controllability and is capable for large area deposition.

vii) Anodic oxidation

The anodization process involves the migration of ions of oxygen, metal, or both depending on the material, through the existing oxide film. Growth rate of an anodic film depends on the current density and the temperature of the electrolyte. Anodic oxidation has been extensively utilized in producing ultra-thin and thick oxide films for tunnel devices, capacitors, protective layers, etc.

viii) Spray Pyrolysis Deposition

The thermal decomposition of a compound to yield a deposit of the stable residue is called pyrolysis. The Spray pyrolysis involves spraying of solution usually aqueous, contained soluble salts of the constituent atoms of the desired compounds on the heated substrates. Chemical pyrolysis method can be defined as a material synthesis, in which the constituents of the vapour phase react to form a solid film at some surface thus; the occurrence of the chemical reaction is an essential characteristic of the pyrolysis method. This method has some similarity to the chemical bath deposition method.
ix) Drop Chemical Deposition

There are two electric heaters with temperature indicator. After preparing the solution, the container is placed and heated on a heater plate until the desired temperature was reached. The substrates were then placed on the other heater plate. The substrate was heated for some time (about one minute) to get steady temperature and then 5 to 6 drops of pre-heated solution are dropped on the heated substrate. The advantage of drop-CD technique includes simplicity, low cost of equipment, better controllability about thickness and capable for large area deposition. Non-conductive substrate (e.g. glass) can be used in this technique.

x) Electrochemical Deposition

Electrochemical (Electrolytic) deposition (ECD) is a technique in which a film of solid metal is deposited from a solution of ions onto an electrically conducting surface. Based on applied electric field across the electrolysis cell, ECD techniques can be classified in three different deposition categories: a) at a constant potential (potentiostatic) b) at a constant current densities (galvanostatic) and c) using periodic pulsed potential (two or three step voltage bias). In case of pulsed deposition, the potential values and duration of time play significant role to control the properties of the deposited films.

For the present work electrodeposition technique is adopted to deposit thin film of copper oxide and is briefed in the following topic.

2.5. Electrodeposition Mechanism

There are different techniques used for the preparation of thin films synthesis of Cu₂O nanostructures by other methods described in the previous part and it requires complex process control, high reaction temperatures, long reaction times, expensive
chemicals and specific method for specific particle size. But, electrochemical method is more advantageous than any other method.

In electrochemical deposition the substrate must be an electrically conductive material. This can be done at low temperature, at low cost, and the films can be prepared for large area and the film quality can be controlled and improved. An electrodeposition is carried out by passing electric current between two or a three electrode with an electrolyte solution containing ions. The working electrode is a cathode, counter electrode is anode and the reference electrode is the saturated electrode. A fixed potential difference is applied between the working electrode and the reference electrode. This potential drives the electrochemical reaction at the working electrode’s surface. The current produced by the electrochemical reaction at the working electrode is balanced by a current flowing in the opposite direction at the counter electrode. The reference electrode establishes a stable potential. The function of the counter electrode is to convert ionic conduction in the electrolyte to electronic conduction by electrochemical reaction.

The chemical reaction consists of two independent half reactions. Each half reaction responds to the interfacial potential difference between the corresponding electrodes. During the first half reaction the deposition occurs in the working electrode. The potential of the working electrode is controlled in the second half using the reference electrode. The potential of the reference electrode is fixed since it has a constant make up. Any potential change in the cell can be described by the working electrode.
Figs. 2.3 (a) Reduction process of a species in solution

Fig. 2.3. (b) Oxidation process of a species in solution

Figs. 2.3 (a) and (b) show how electrochemical reaction occurs when potential is applied to the working electrode. When a negative potential is given to the working electrode, the energy of the electrode in it is increased. When the energy of the
electron in the working electrode is greater than the vacant electronic energy states on the species in the electrolyte, electrons will flow from working electrode into the solution. This produces a cathodic current and this causes reduction of the species in the solution at the surface of the working electrode. Similarly when the positive potential is applied, energy of the electrons in the working electrode will be lowered. At certain point, electrons will flow from solution species to working electrode and form an anodic current, which results in the oxidation of the species in the solution. The critical point at which the reaction happens is called the saturated potential $E^*$ for the related species in the solution. But the electrode reaction will not only be controlled by the applied potential but also by many other factors like mass transfer, reactive species to electrode surface, electron transfer at the electrode surface, chemical reaction etc.

In the electrodeposition, the reactant dissolved in the electrolyte is deposited as a solid product. For the deposition of thin films on the working electrode a particular potential is given to the working electrode with respect to the reference electrode. The cell current decreases rapidly as the reaction proceeds due to low rates of diffusion of the reactant molecules to the electrodes. Also the activity of the reactant decreases.

From the thermodynamics point of view, an electrochemical reaction is simple, while practically, it’s much more complicated. An electrode reaction is a heterogeneous reaction since it happens at the interface between the electrode and electrolyte. Therefore, an electrode reaction will not only be controlled by applied potential but also by many other factors like current density, bath composition, pH of the electrolyte, temperature of the bath and electrode shape. If proper potential is
given pure a single phase product can be obtained. For the present work three electrode cell is used and is briefed in the next chapter.

2.6. SILAR method

One of the new methods for the deposition of thin film is successive ionic layer adsorption and reaction also known as SILAR method. This method was first reported by Ristov et al., in 1985. In general, the SILAR growth cycle contains four different steps: adsorption, rinsing, reaction and rinsing.

Adsorption: The collection of a substance on the surface of another substance is known as adsorption, which is the fundamental building block of the SILAR method. Here, the cations present in the precursor solution are adsorbed on the surface of the substrate and form the Helmholtz electric double layer. Adsorption is an exothermic process. The adsorption is a surface phenomenon between ions and surface of substrate and is possible due to attraction force between ions in the solution and surface of the substrate. The absorbed layer is composed of two layers: the inner (positively charged) and outer (negatively charged) layers. The positive layer consists of the cations and the negative form the counter ions of the cations.

Rinsing (I): In this step, excess adsorbed ions, are rinsed away from the diffusion layer. This results into saturated electrical double layer.

Reaction: In this reaction step, the anions from anionic precursor solution are introduced to the system. Due to the low stability of the material, a solid substance is formed on the interface.

Rinsing (II): In last step of the SILAR cycle, the excess and unreacted species and the reaction by product from the diffusion layer are removed.
Rinsing follows each reaction, which enables heterogeneous reaction between the solid phase and the solvated ions in the solution.


After having reviewed and analysed the structure and method of preparation of copper oxide thin films the preparation of the same is carried out and is discussed in the next chapter.
References


Diwakar Chauhan, Satsangi, V.R., Sahab Dass and Rohit Shrivastav, 2006. Preparation and characterization of nanostructured CuO thin films for


Madelung, O., Semiconductors Basic Data, 1996. Springer-Verlag, Germany, 11.


