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Cuprous Oxide as an Active Material for Solar Cells

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1. Introduction

Growing demand for energy sources that are cleaner and more economical led to intensive research on alternative energy sources such as rechargeable lithium batteries and solar cells, especially those in which the sun's energy is transformed into electrical or chemical. From the ecology point of view, using solar energy does not disturb the thermal balance of our planet, either being directly converted into heat in solar collectors or being transformed into electrical or chemical energy in solar cells and batteries. On the other hand, every kilowatt hour of energy thus obtained replaces a certain amount of fossil or nuclear fuel and mitigates any associated adverse effects known. Solar energy is considered to be one of the most sustainable energy resources for future energy supplies.

To make the energy of solar radiation converted into electricity, materials that behave as semiconductors are used. Semiconductive properties of copper sulfides and copper oxides, as well as compounds of chalcopyrite type have been extensively investigated (Rajčić-Vujasinović et al., 1994, 1999). One of the important design criteria in the development of an effective solar cell is to maximize its efficiency in converting sunlight to electricity. A photovoltaic cell consists of a light absorbing material which is connected to an external circuit in an asymmetric manner. Charge carriers are generated in the material by the absorption of photons of light, and are driven towards one or other of the contacts by the built-in spatial asymmetry. This light driven charge separation establishes a photo voltage at open circuit, and generates a photocurrent at short circuit. When a load is connected to the external circuit, the cell produces both current and voltage and can do electrical work.

Solar technology, thanks to its advantages regarding the preservation of the planetary energy balance, is getting into an increasing number of application areas. So, for example, Rizzo et al. (2010) as well as Stević & Rajčić-Vujasinović (in Press) describe hybrid solar vehicles, while Vieira & Mota (2010) show a rechargeable battery with photovoltaic panels.

The high cost of silicon solar cells forces the development of new photovoltaic devices utilizing cheap and non-toxic materials prepared by energy-efficient processes. The Cu–O system has two stable oxides: cupric oxide (CuO) and cuprous oxide (Cu_2O). These two oxides are semiconductors with band gaps in the visible or near infrared regions. Copper and copper oxide (metal-semiconductor) are one of the first photovoltaic cells invented (Pollack and Trivich, 1975). Cuprous oxide (Cu_2O) is an attractive semiconductor material that could be used as anode material in thin film lithium batteries (Lee et al, 2004) as well as in solar cells (Akimoto et al., 2006; Musa et al., 1998; Nozik et al., 1978; Tang et al., 2005). Its semiconductor properties and the emergence of photovoltaic effect were discovered by Edmond Becquerel 1839th[1] experimenting in the laboratory of his father, Antoine-César Becquerel.

Cu_2O is a p-type semiconductor with a direct band gap of 2.0–2.2 eV (Grozdanov, 1994) which is suitable for photovoltaic conversion. Tang et al. (2005) found that the band gap of nanocrystalline Cu_2O thin films is 2.06 eV, while Siripala et al. (1996) found that the deposited cuprous oxide exhibits a direct band gap of 2.0 eV, and shows an n-type behavior when used in a liquid/solid junction. Han & Tao (2009) found that n-type Cu_2O deposited in a solution containing 0.01 M copper acetate and 0.1 M sodium acetate exhibits higher resistivity than p-type Cu_2O deposited at pH 13 by two orders of magnitude. Other authors, like Singh et al. (2008) estimated the band gap of prepared Cu_2O nanothreads and nanowires to be 2.61 and 2.69 eV, which is larger than the direct band gap (2.17 eV) of bulk Cu_2O (Wong & Searson, 1999). The higher band gap can be attributed to size effect of the present nanostructures. Thus the increase of band gap as compared to the bulk can be understood on the basis of quantum size effect which arises due to very small size of nanothreads and nanowires in one-dimension.

Cuprous oxide attracts the most interest because of its high optical absorption coefficient in the visible range and its reasonably good electrical properties (Musa et al., 1998). Its advantages are, in fact, relatively low cost and low toxicity. Except for a thin film that can be electrochemically formed on different substrates (steel, TiO_2), cuprous oxide can be obtained in the form of nano particles with all the benefits offered by nano-technology (Daltin et al., 2005; Zhou & Switzer, 1998). Nanomaterials exhibit novel physical properties and play an important role in fundamental research.

The unit cell of Cu_2O with a lattice constant of 0.427 nm is composed of a body centered cubic lattice of oxygen ions, in which each oxygen ion occupies the center of a tetrahedron formed by copper ions (Xue & Dieckmann, 1990). The Cu atoms arrange in a fcc sublattice, the O atoms in a bcc sublattice. The unit cell contains 4 Cu atoms and 2 O atoms. One sublattice is shifted by a quarter of the body diagonal. The space group is Pn3m, which includes the point group with full octahedral symmetry. This means particularly that parity is a good quantum number. Figure 1 shows the crystal lattice of Cu_2O. Molar mass of Cu_2O is 143.09 g/mol, density is 6.0 g/cm^3 and its melting and boiling points are 1235°C and 1800°C, respectively. Also, it is soluble in acid and insoluble in water.

Cuprous oxide (copper (I) oxide Cu_2O) is found in nature as cuprite and formed on copper by heat. It is a red color crystal used as a pigment and fungicide. Rectifier diodes based on this material have been used industrially as early as 1924, long before silicon became the standard. Cupric oxide (copper(II) oxide CuO) is a black crystal. It is used in making fibers and ceramics, gas analyses and for Welding fluxes. The biological property of copper compounds takes important role as fungicides in agriculture and biocides in antifouling paints for ships and wood preservations as an alternative of Tributyltin compounds.

In solar cells, Cu_2O has not been commonly used because of its low energy conversion efficiency which results from the fact that the light generated charge carriers in micron-sized Cu_2O grains are not efficiently transferred to the surface and lost due to recombination. For randomly generated charge carriers, the average diffusion time from the bulk to the surface is given by:

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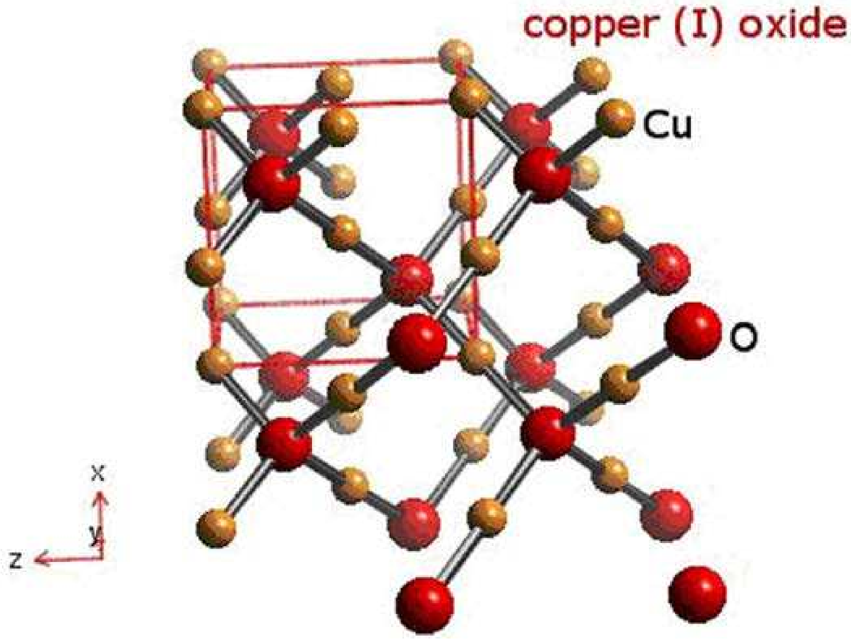
[1] http://pvcdrom.pveducation.org/MANUFACT/FIRST.HTM

$$\tau = r^2 / \pi^2 D \tag{1}$$

where r is the grain radius and D is the diffusion coefficient of the carrier (Rothenberger et al., 1985, as cited in Tang et al., 2005). If the grains radius is reduced from micrometer dimensions to nanometer dimensions, the opportunities for recombination can be dramatically reduced. The preparation of nano crystalline Cu_2O thin films is a key to improving the performance of solar application devices. Nanotechnologies in this area, therefore, given their full meaning. In the last decade the scientific literature, abounds with works again showing progress in research related to obtaining the cuprous oxide.



(http://www.webelements.com/compounds/copper/dicopper_oxide.html)

Fig. 1. Crystal structure of Cu_2O

This chapter presents an overview of recent literature concerning cuprous oxide synthesis and application as an active material in solar cells, as well as our own results of synthesis and investigations of Cu_2O thin films using electrochemical techniques.

2. Methodologies used for the synthesis of cuprous oxide

The optical and electrical properties of absorber materials in solar cells are key parameters which determine the performance of solar cells. Hence, it is necessary to tune these properties properly for high efficient device. Electrical properties of Cu_2O, such as carrier mobility, carrier concentration, and resistivity are very dependent on preparation methods.

Cuprous oxide thin films have been prepared by various techniques like thermal oxidation (Jayatissa et al., 2009; Musa et al., 1998; Sears & Fortin, 1984), chemical vapor deposition (Kobayashi et al. 2007; Maruyama, 1998; Medina-Valtierra et al., 2002; Ottosson et al., 1995; Ottosson & Carlsson, 1996), anodic oxidation (Fortin & Masson, 1982; Sears and Fortin, 1984; Singh et al., 2008), reactive sputtering (Ghosh et al., 2000), electrodeposition (Briskman, 1992; Daltin et al., 2005; Georgieva & Ristov, 2002; Golden et al., 1996; Liu et al., 2005; Mizuno et al., 2005; Rakhshani et al., 1987, Rakhshani & Varghese, 1987; Santra et al., 1999; Siripala et al., 1996; Tang et al., 2005; Wang et al., 2007; Wijesundera et al., 2006), plasma evaporation (Santra et al., 1992), sol–gel-like dip technique (Armelao et al., 2003; Ray, 2001) etc. Each of these methods has its own advantages and disadvantages. In most of these studies, a mixture of phases of Cu, CuO and Cu_2O is generally obtained and this is one of the nagging problems for non-utilizing Cu_2O as a semiconductor (Papadimitropoulos et al., 2005). Pure Cu_2O films can be obtained by oxidation of copper layers within a range of temperatures followed by annealing for a small period of time.

Results obtained using different methods, especially thermal oxidation and chemical vapor evaporation for synthesis of cuprous oxide thin films, are presented in next sections, with special emphasis on the electrochemical synthesis of cuprous oxide.

2.1 Thermal oxidation

Polycrystalline cuprous oxide can be formed by thermal oxidation of copper under suitable conditions (Rai, 1988). The procedure involves the oxidation of high purity copper at an elevated temperature (1000–1500^{0}C) for times ranging from few hours to few minutes depending on the thickness of the starting material (for total oxidation) and the desired thickness of Cu_2O (for partial oxidation). Process is followed by high-temperature annealing for hours or even days.

Sears & Fortin (1984) synthesized cuprous oxide films on copper substrates to a thickness of a few micrometers, using both thermal and anodic oxidation techniques. The measurements carried out on the anodic oxide layers indicate an unwanted but inevitable incorporation of other compounds into the Cu_2O. They found that the photovoltaic properties of the resulting Cu_2O/Cu backwall cells depend critically on the copper surface preparation, as well as on the specific conditions of oxidation. Backwall cells of the thermal variety with thicknesses down to 3 μm do not quite yet approach the performance of the best Cu_2O 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_2O 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.

Musa et al. (1998) produced the cuprous oxide by thermal oxidation and studied its physical and electrical properties. The oxidation was carried out at atmospheric pressure in a high-temperature tube furnace. During this process the copper foils were heated in the range of 200 to 1050°C. Cu_2O has been identified to be stable at limited ranges of temperature and oxygen pressure. It has also been indicated that during oxidation, Cu_2O is formed first, and after a sufficiently long oxidation time CuO is formed (Roos & Karlson, 1983, as cited Musa et al., 1998). It has been suggested that the probable reactions that could account for the presence of CuO in layers oxidised below 1000 °C are:

$$2Cu_2O + O_2 \rightarrow 4CuO \tag{2}$$

$$Cu_2O \rightarrow CuO + Cu \tag{3}$$

The unwanted CuO can be removed using an etching solution consisting of FeCl, HCl, and 8 M HNO_3 containing NaCl. The results of the oxidation process as deduced from both XRD and SEM studies indicate that the oxide layers resulting from oxidation at 1050^{0}C consist entirely of Cu_2O. Those grown below 1040^{0}C gave mixed oxides of Cu_2O and CuO. It was observed that in general the lower the temperature of oxidation, the lower the amount of Cu_2O was present in the oxide. Thermodynamic considerations indicate that the limiting temperature for the elimination of CuO from the oxide layer was found to be 1040^{0}C. For thermal oxidation carried out below 1040^{0}C, Cu_2O is formed first and it is then gradually oxidised to CuO depending on the temperature and time of reaction. Pure unannealed Cu_2O layers grown thermally in air are observed to exhibit higher resistivity and low hole mobility. A significant reduction in resistivity and an increase in mobility values were obtained by oxidizing the samples in the presence of HCl vapour, followed by annealing at 500^{0}C. Cu_2O layers grown in air without the annealing process gave resistivities in the range $2x10^3$ – $3x10^3$ Ωcm. A substantial reduction in the resistivity of the samples was achieved by doping with chlorine during growth and annealing. An average mobility of 75 cm^2 V^{-1} s^{-1} at room temperature was obtained for eight unannealed Cu_2O samples. This average value increased to 130 cm^2 V^{-1} s^{-1} after doping the samples with chlorine and annealing. The SEM studies indicate that the annealing process results in dense polycrystalline Cu_2O layers of increased grain sizes which are appropriate for solar-cell fabrication. Figure 2 presents the micrograph of the surface morphology of a copper foil partially oxidised at 970^{0}C for 2 min. The sample was neither annealed nor etched. The surface shows the black CuO coat formed on the violet-red Cu_2O after the oxidation process. The surface morphology is porous and amorphous in nature. The structure formed by this oxidation process is of the form $CuO/Cu_2O/Cu/Cu_2O/CuO$.

Jayatissa et al. (2009) prepared cuprous oxide (Cu_2O) 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_2O and CuO was controlled by varying oxidation conditions such as oxygen partial pressure, heat treatment temperature and oxidation time. Authors used X-ray diffraction, atomic force microscopy and optical spectroscopy to determinate the microstructure, crystal direction, and optical properties of copper oxide films. The experimental results suggest that the thermal oxidation method can be employed to fabricate device quality Cu_2O and CuO films that are up to 200–300 nm thick.

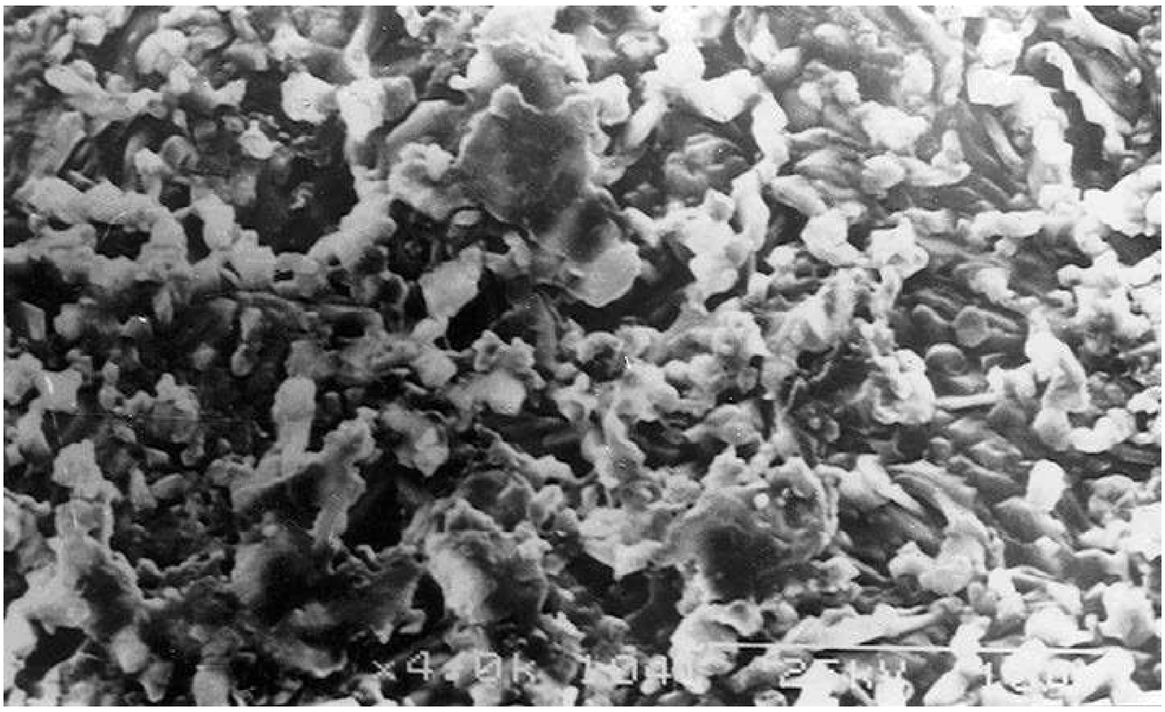


Fig. 2. SEM micrograph of unetched and unannealed sample oxidised at 970^{0}C for 2 min showing CuO coating (Musa et al., 1998)

2.2 Chemical vapor deposition

Chemical vapor deposition is a chemical process used to produce high-purity, high-performance solid materials. The films may be epitaxial, polycrystalline or amorphous depending on the materials and reactor conditions. Chemical vapor deposition has become the major method of film deposition for the semiconductor industry due to its high throughput, high purity, and low cost of operation. Several important factors affect the quality of the film deposited by chemical vapor deposition such as the deposition temperature, the properties of the precursor, the process pressure, the substrate, the carrier gas flow rate and the chamber geometry.

Maruyama (1998) prepared polycrystalline copper oxide thin films at a reaction temperature above 280^{0}C by an atmospheric-pressure chemical vapor deposition method. Copper oxide films were grown by thermal decomposition of the source material with simultaneous reaction with oxygen. At a reaction temperature above 280^{0}C, polycrystalline copper oxide films were formed on the borosilicate glass substrates. Two kinds of films, i.e., Cu_2O and CuO, were obtained by adjusting the oxygen partial pressure. Also, there are large differences in color and surface morphology between the CuO and Cu_2O films obtained. Author found that the surface morphology and the color of CuO film change with reaction temperature. The CuO film prepared at 300^{0}C is real black, and the film prepared at 500^{0}C is grayish black.

Medina-Valtierra et al. (2002) coated fiber glass with copper oxides, particularly in the form of $6CuO{\bullet}Cu_2O$ by chemical vapor deposition method. The authors' work is based on design of an experimental procedure for obtaining different copper phases on commercial fiberglass. Films composed of copper oxides were deposited over fiberglass by sublimation and transportation of $(acac)_2Cu(II)$ with a O_2 flow (oxidizing agent), resulting in the decomposition of the copper precursor, deposition of Cu^0 and Cu^0 oxidation on the fiberglass over a short range of deposition temperatures. The copper oxide films on the fiberglass were examined using several techniques such as X-ray diffraction (XRD), visible spectrophotometry, scanning electronic microscopy (SEM) and atomic force microscopy (AFM). The films formed on fiberglass showed three different colors: light brown, dark brown and gray when Cu_2O, $6CuO{\bullet}Cu_2O$ or CuO, respectively, were present. At a temperature of 320°C only cuprous oxide is formed but at a higher temperature of about 340°C cupric oxide is formed. At a temperature of 325°C $6CuO\text{-}Cu_2O$ is formed. The decomposition of precursor results in the formation of a zero valent copper which upon oxidation at different temperature gives different oxides.

Ottosson et al. (1995) deposited thin films of Cu_2O onto MgO (100) substrates by chemical vapour deposition from copper iodide (CuI) and dinitrogen oxide (N_2O) at two deposition temperatures, 650°C and 700°C. They found that the pre-treatment of the substrate as well as the deposition temperature had a strong influence on the orientation of the nuclei and the film. For films deposited at 650°C several epitaxial orientations were observed: (100), (110) and (111). The Cu_2O(100) was found to grow on a defect MgO(100) surface. When the substrates were annealed at 800°C in N_2O for 1 h, the defects in the surface disappeared and only the (110) orientation was developed during the deposition. The films deposited at 700°C (without annealing of the substrates) displayed only the (110) orientation.

Markworth et al. (2001) prepared cuprous oxide (Cu_2O) films on single-crystal MgO(110) substrates by a chemical vapor deposition process in the temperature range 690–790°C. Cu_2O (a=0.4270 nm) and MgO (a=0.4213 nm) have cubic crystal structures, and the lattice mismatch between them is 1.4%. Due to good lattice match, chemical stability, and low cost, MgO single crystals are particularly effective substrates for the growth of Cu_2O thin films. Authors found that the Cu_2O films grow by an island-formation mechanism on MgO substrate. Films grown at 690°C uniformly coat the substrate except for micropores between grains. However, at a growth temperature of 790°C, an isolated, three-dimensional island morphology develops.

Kobayashi et al. (2007) investigated the high-quality Cu_2O thin films grown epitaxially on MgO (110) substrate by halide chemical vapor deposition under atmospheric pressure. CuI in a source boat was evaporated at a temperature of 883 K, and supplied to the growth zone of the reactor by N_2 carrier gas, and O_2 was also supplied there by the same carrier gas. Partial pressure of CuI and O_2 were adjusted independently to 1.24×10^{-2} and 1.25×10^3 Pa. They found that the optical band gap energy of Cu_2O film calculated from absorption spectra is 2.38 eV. The reaction of CuI and O_2 under atmospheric pressure yields high-quality Cu_2O films.

2.3 Other methods

Several novel methods for the synthesis of cuprous oxide (i.e. reactive sputtering, sol-gel technique, plasma evaporation,) and some results obtained using these techniques are presented in this part. For example, Santra et al. (1992) deposited thin films of cuprous oxide on the substrates by evaporating metallic copper through a plasma discharge in the presence of a constant oxygen pressure. Authors found two oxide phases before and after annealing treatment of films. Before annealing treatment, cuprous oxide was identified and after annealing in a nitrogen atmosphere, cuprous oxide changes to cupric oxide. The results of optical absorption measurement show that the band gap energies for Cu_2O and CuO are 2.1 eV and 1.85 eV, respectively. Thin films prepared in the absence of a reactive gas and plasma were also deposited on glass substrates and in these films the presence of metallic copper was identified.

Ghosh et al. (2000) deposited cuprous oxide and cupric oxide by RF reactive sputtering at different substrate temperatures, namely, at 30, 150 and 300^0C. They used atomic force microscopy for examination of the properties of the prepared oxides films related to surface morphology. It was found for the film deposited at 30^0C, that, 8-10 small grains of size ~40 nm diameter agglomerate together and make a big grain of size ~120 nm. At the temperature of 150^0C the grain size becomes 160 nm. The grain size decreases to 90 nm at 300^0C. 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 temperature corresponding to 30, 150 and 300^0C, respectively. Optical band gap of the films deposited at 30, 150 and 300^0C are 1.75, 2.04 and 1.47 eV, respectively. Different phases of copper oxides are found at different temperatures of deposition. CuO phase is obtained in the films prepared at a substrate temperature of 300^0C.

Sol gel-like dip technique is a very simple and low-cost method, which requires no sophisticated specialized setup. For example, Armelao et al. (2003) used a sol-gel method to synthesize nanophasic copper oxide thin films on silica slides. They used copper acetate monohydrate as a precursor in ethanol as a solvent. Authors observed formation of CuO crystallites in the samples annealed under inert atmosphere (N_2) up to 3 h. A prolonged treatment (5 h) in the same environment resulted in the complete disappearance of tenorite and in the formation of a pure cuprite crystalline phase. Also, under reducing conditions, the formation of CuO, Cu_2O and Cu was progressively observed, leading to a mixture of Cu(II) and Cu(I) oxides and metallic copper after treatment at 900^0C for 5 h.

All the obtained films have nanostructure with an average crystallite size lower than 20 nm.

Nair et al. (1999) deposited cuprous oxide thin films on glass substrate using chemical technique. The glass slides were dipped first in a 1 M aqueous solution of NaOH at the temperature range 50-90°C for 20 s and then in a 1 M aqueous solution of copper complex. X-ray diffraction patterns showed that the films, as prepared, are of cuprite structure with composition Cu_2O. Annealing the films in air at 350^0C converts these films to CuO. This conversion is accompanied by a shift in the optical band gap from 2.1 eV (direct) to 1.75 eV (direct). The films show p-type conductivity, $\sim 5 \times 10^{-4}\ \Omega^{-1}\ cm^{-1}$ for a film of thickness 0.15 µm.

3. Electrochemical synthesis

3.1 Electrodeposition

Synthesis of Cu_2O nanostructures by the methods described in the previous part demands complex process control, high reaction temperatures, long reaction times, expensive chemicals and specific method for specific nanostructures. A request for obtaining nanometer particles, cause complete change of technology in which Cu_2O is formed on the cathode by reduction of Cu^{2+} ions from the organic electrolyte. The possible reactions during the cathodic reduction of copper (II) lactate solution are:

$$2Cu^{2+} + H_2O + 2e^{-} = Cu_2O + 2H^{+} \tag{4}$$

$$Cu^{2+} + 2e^{-} = Cu \tag{5}$$

$$Cu_2O + 2H^{+} + 2e^{-} = 2Cu + H_2O \tag{6}$$

The electrodeposition techniques are particularly well suited for the deposition of single elements but it is also possible to carry out simultaneous depositions of several elements and syntheses of well-defined alternating layers of metals and oxides with thicknesses down to a few nm. So, electrodeposition is a suitable method for the synthesis of semiconductor thin films such as oxides. This method provides a simple way to deposit thin Cu(I) oxide films onto large-area conducting substrates (Lincot, 2005). Thus, the study of the growth kinetics of these films is of considerable importance. In this section we present some results of electrochemical deposition of cuprous oxide obtained by various authors.

Rakhshani 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_2O 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_2O with no traces of CuO. The optical band gap for electrodeposited Cu_2O films was 1.95 eV. Deposition temperature played an important role in the size of deposited grains. Films were photoconductive with high dark resistivities. Also, Rakhshani & Varghese (1987) electrodeposited cuprous oxide thin films galvanostatically on 0.05 mm thick stainless steel substrates at a temperature of 60^0C. The deposition solution with pH 9 consisted of lactic acid (2.7 M), anhydrous cupric sulphate (0.4 M), and sodium hydroxide (4 M). Authors found that all the films deposited at 60 °C consisted only of Cu_2O 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) deposited Cu_2O films by galvanostatic method on copper substrates. An alkaline cupric sulphate (about 0.3 M) bath containing NaOH (about 3.2 M) and lactic acid (about 2.3 M) was used as the electrolyte at pH 9. The bath temperatures were 40, 50 and 60°C. XRD analysis indicated a preferred (200) orientation of the Cu_2O deposited film. The deposition kinetics was found to be independent of deposition temperature and linear in the thickness range studied (up to about 20 μm). The electrical conductivity of Cu_2O films was found to vary exponentially with temperature in the 145-300^{0}C range with associated activation energy of 0.79 eV.

Golden et al. (1996) found that the reflectance and transmittance of the electrodeposited films of cuprous oxide give a direct band gap of 2.1 eV. Namely, 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). Films were deposited onto either stainless steel or indium tin oxide (ITO) substrates. 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_2O 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 pH 9 the orientation of the film is [100], while at a solution pH 12 the orientation changes to [111]. The degree of [111] texture for the films grown at pH 12 increased with applied current density.

Siripala et al. (1996) deposited cuprous oxide films on indium tin oxide (ITO) coated glass substrates in a solution of 0.1 M sodium acetate and 1.6×10^{-2} M cupric acetate and the effect of annealing in air has been studied too. Electrodeposition was carried out for 1.5 h in order to obtain films of thicknesses in the order of 1 μm. Authors concluded that the electrodeposited Cu_2O films are polycrystalline with grain sizes in the order of 1-2 μm and the bulk crystal structure is simple cubic. They concluded that there is no apparent change in the crystal structure when heat treated in air at or below 300°C. Annealing in air changes the morphology of the surface creating a porous nature with ring shaped structures on the surface. Annealing above 300°C causes decomposition of the yellow-orange colour Cu_2O film into a darker film containing black CuO and its complexes with water.

Zhou & Switzer (1998) deposited Cu_2O films on stainless steel disks by the cathodic reduction of copper (II) lactate solution (0.4 M cupric sulfate and 3 M lactic acid). The pH of the bath was between 7 and 12 and the bath temperature was 60°C. Authors concluded that the preferred orientation and crystal shape of Cu_2O films change with the bath pH and the applied potential. They obtained pure Cu_2O films at bath pH 9 with applied potential between -0.35 and -0.55 (SCE) or at bath pH 12.

Mahalingam et al. (2000) deposited cuprous oxide thin films on copper and tin-oxide-coated glass substrates by cathodic reduction of alkaline cupric lactate solution (0.45 M $CuSO_4$, 3.25 M lactic acid and 0.1 M NaOH). The deposition was carried out in the temperature range of 60-80^{0}C at pH 9. Galvanostatic deposition on tin-oxide-coated glass and copper substrates yields reddish-grey Cu_2O 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 gap of 1.99 eV, and extinction coefficient of 0.195. After deposition on temperature of 70^{0}C, cuprous oxide films were annealed in air for 30 min at different temperatures (150, 250 and 350^{0}C) to obtain their room temperature resistivity. It showed a decrease in resistivity of Cu_2O film of the order of 10^7 Ωcm to 10^4 Ωcm. The explanation of such behavior may be due to increase in hole conduction.

Georgieva & Ristov (2002) deposited the cuprous oxide (Cu_2O) films using a galvanostatic method from an alkaline $CuSO_4$ bath containing lactic acid and sodium hydroxide (64 g/l anhydrous cupric sulphate ($CuSO_4$), 200 ml/l lactic acid ($C_3H_6O_3$) and about 125 g/l sodium hydroxide (NaOH)). The electrodeposition temperature was 60^{0}C. Authors obtained polycrystalline films of 4–6 µm in thickness with optical band gap of 2.38 eV.

Daltin et al. (2005) applied potentiostatic deposition method to obtain cuprous oxide nanowires in polycarbonate membrane by cathodic reduction of alkaline cupric lactate solution (0.45 M Cu(II) and 3.25 M lactate). Authors found that the optimum electrochemical parameters for the deposition of nanowires are: pH 9.1, temperature 70^{0}C, and applied potential -0.9 V (SSE). The morphology of the nanowires was analyzed by SEM. The obtained nanowires had uniform diameters of about 100 nm and lengths up to 16 µm. Scanning electron micrograph of electrodeposited Cu_2O nanowires are presented in Figure 3.

Liu et al. (2005) investigated the electrochemical deposition of Cu_2O films onto 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, electrical current increases gradually during deposition, while for the films growth 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_2O film formation. Cu_2O crystals with microsized pyramidal shape were grown on ITO substrate. Nanosized and pyramidal shaped Cu_2O particles were formed on Si substrate and the film grown on Au substrate shows a (100) orientation with much better crystallinity.

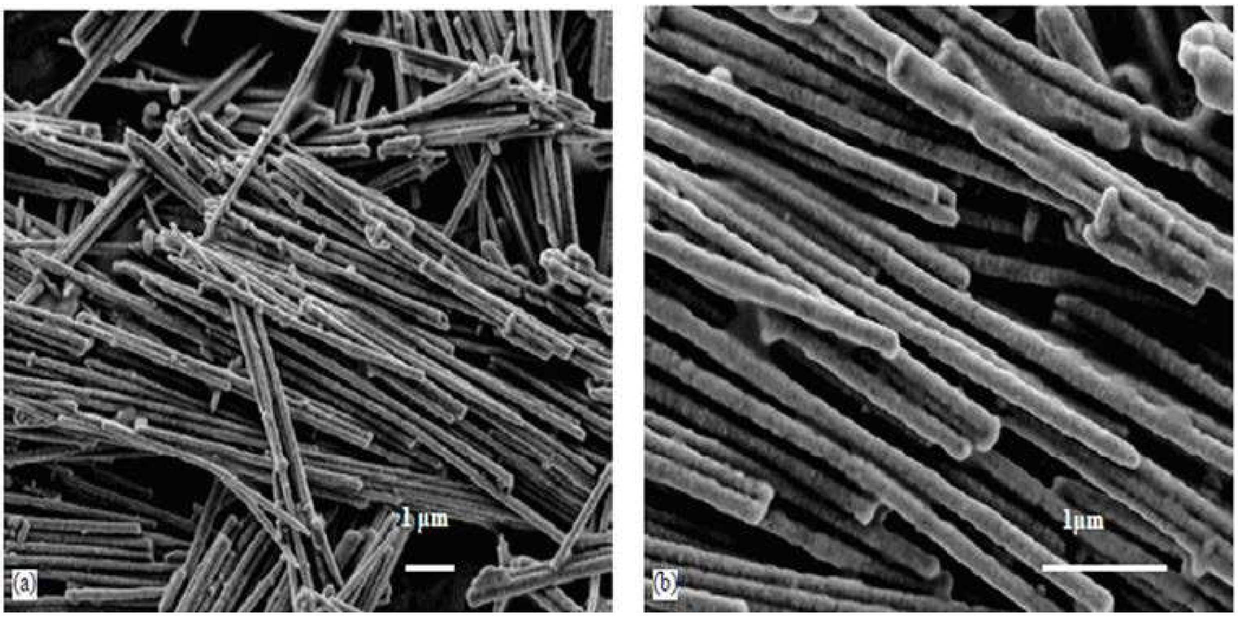


Fig. 3. (a) Scanning electron micrograph of electrodeposited Cu_2O nanowires. Bath temperature 70^{0}C, pH 9.1, E -1.69 V/$_{SSE}$. (b) Enlarged (a) (Daltin et al., 2005)

Tang et al. (2005) investigated the electrochemical deposition of nanocrystalline Cu_2O 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_2O thin films. The effect of bath pH on electrodeposition of Cu_2O thin film was investigated by selecting a bath temperature of 30^0C and an applied potential of -245 mV (SCE). Authors found that the films deposited at pH 4 are mostly metallic Cu and only little Cu_2O. In the region of pH 4 to pH 5.5, the deposited films are a composite of Cu and Cu_2O, while the films deposited at pH between 5.5 and 6 are pure Cu_2O. Pure Cu_2O deposited at bath temperature between 0 and 30^0C produced spherically shaped grains with 40~50 nm in diameter. The bath temperature must be controlled in the range of 0-30^0C to obtain nanocrystalline Cu_2O thin film. At a temperature of 45°C, a highly branched dendrite formed, and the grain size increased to 200–500 nm. At the temperature above 60°C, a ring-shaped structure with a porous surface was observed. Optical absorption measurements indicate that annealing at 200^0C can improve the transmittance of the nanocrystalline Cu_2O thin films. Figure 4 shows SEM photographs of Cu_2O films deposited at various bath temperatures.

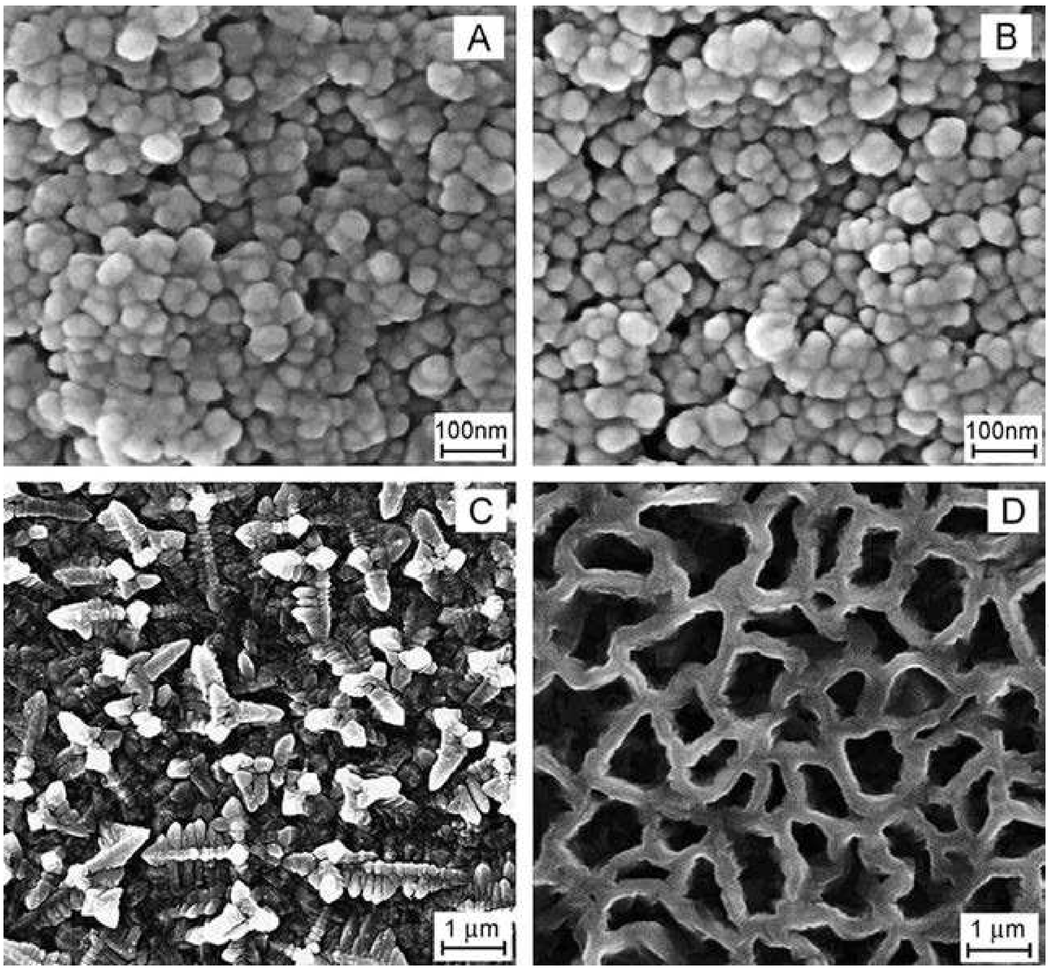


Fig. 4. SEM photographs of Cu_2O films deposited at various bath temperatures: (A) 0^0C, (B) 30^0C, (C) 45^0C, and (D) 60^0C (Tang et al., 2005)

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_2O can be deposited from 0 to -300 mV (SCE). Also, co-deposition of Cu and Cu_2O starts at - 400 mV (SCE). At the deposition potential from -700 mV (SCE) a single phase Cu thin films are produced. Single phase polycrystalline Cu_2O thin films with cubic grains of 1–2 µm can be possible at the deposition potential around -200 mV (SCE).

Wang et al. (2007) cathodically electrodeposited cuprous oxide films from 0.4 M copper sulfate bath containing 3 M lactic acid. The bath pH was carefully adjusted between 7.5 and 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 examinated. Authors found that three orientations, namely, (100), (110), and (111) dominate as the bath pH is increased from ~ 7.5 to ~ 12.

Recently, Hu et al. (2009) electrodeposited Cu_2O thin films onto 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_2O 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_2O thin films produced in the alkaline electrolyte has a typical pyramid shape. The electrocrystallization mechanisms are considered to be related to the nucleation rate, cluster growth, and crystal growth. To investigate the initial stage of nucleation and cluster growth, different current densities with the same deposition time were applied. Figure 5 shows that a relatively large cluster size and a relatively small number of nucleation sites were obtained under a current density of 1 $mAcm^{-2}$. At a high current density of 5 $mAcm^{-2}$, more nucleation sites and a small cluster size were obtained.

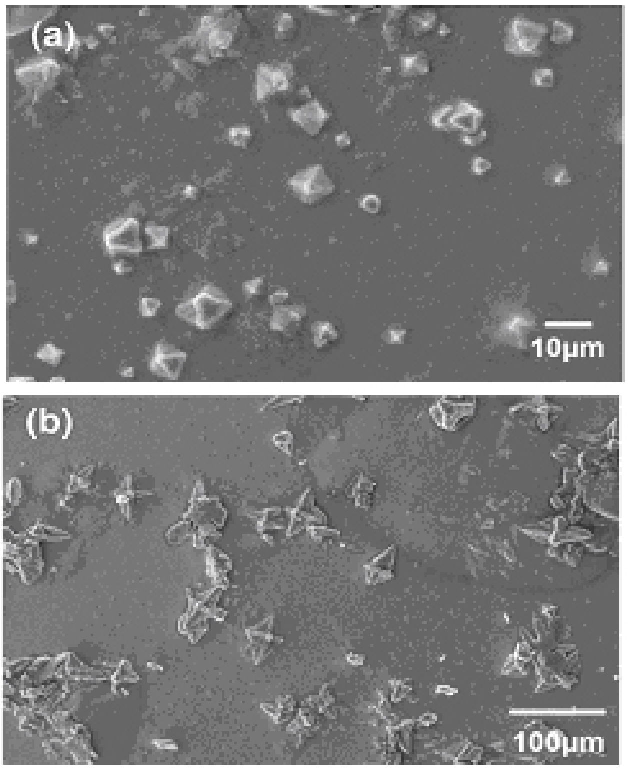


Fig. 5. The Cu_2O films synthesized under different current densities with the same deposition time (Hu et al., 2009)

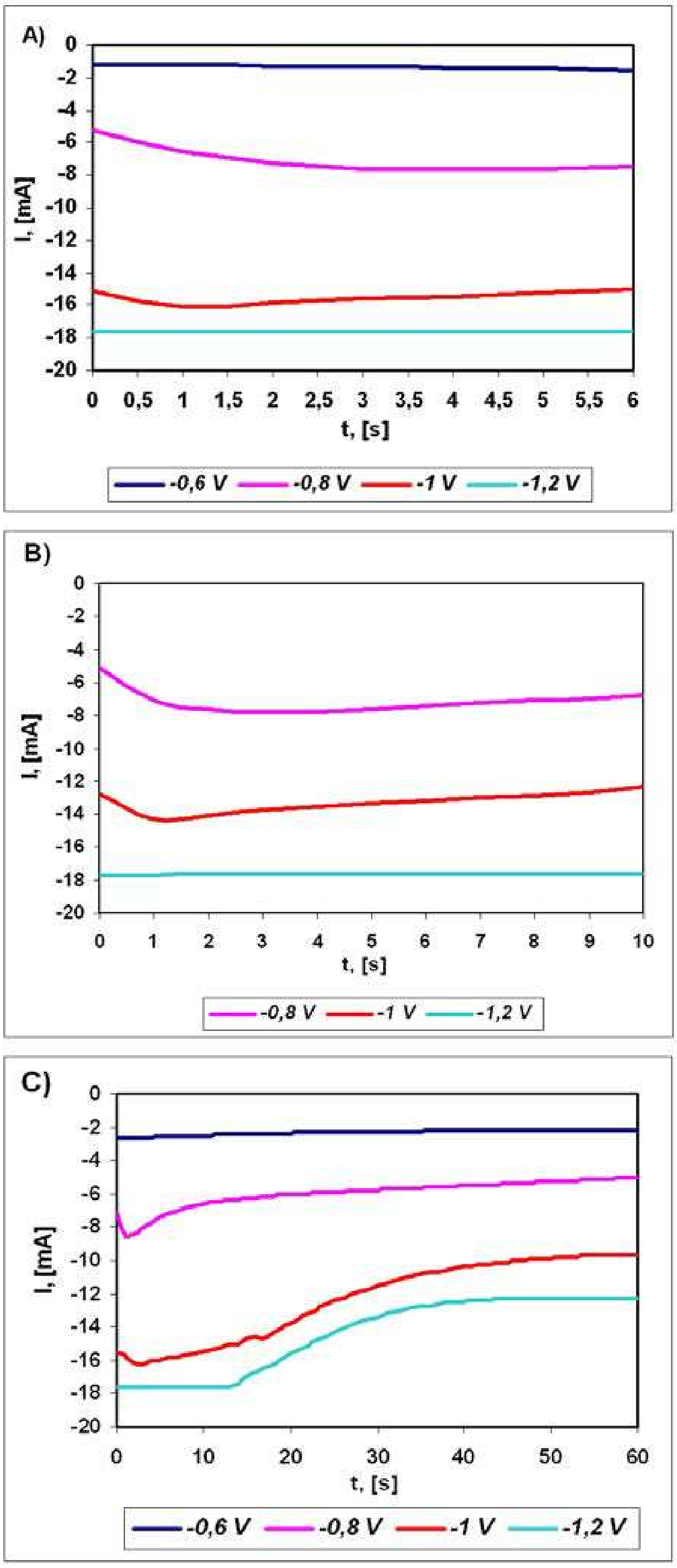


Fig. 6. Current density vs. time curves for electrodeposition of Cu_2O thin film on titanium electrode (electrodeposition time: (A) 6 s, (B) 10 s and (C) 60 s; t = 25 ºC, pH 9.22)

Bugarinović et al. (2009) investigated the electrochemical deposition of thin films of cuprous oxide on three different substrates (stainless steel, platinum and copper). All experiments of Cu_2O thin films deposition were performed at room temperature. Using experimental technique described elsewhere (Stević & Rajčić-Vujasinović, 2006; Stević & et al., 2009), electrodeposition was carried out in in a copper lactate solution as an organic electrolyte (0.4 M copper sulfate and 3 M lactic acid, pH 7-10 is set using NaOH). The conditions are adjusted so that the potentials which arise Cu_2O and CuO are as different as possible. Characterization of obtained coatings was performed by cyclic voltammetry. The results indicate that the composition of the substrate strongly affects electrochemical reactions. Reaction with the highest rate took place on a copper surface, while the lowest rate was obtained on the platinum electrode. The results show that the co-deposit of Cu_2O and Cu was obtained at - 800 mV (SCE) on stainless steel electrode. The same authors investigated the electrodeposition of cuprous oxide thin film on titanium electrode. The obtained results are presented in Figure 6.

Cuprous oxide thin films were deposited at potentials -0.6 V, -0.8 V, -1.0 V and 1.2 V with respect to SCE. All experiments were carried out for a duration of 6 s, 10 s and 1 minute. When the electrodeposition lasted 6 s (Fig. 6A), obtained currents depended on applied potentials. Lowest current of 1mA was obtained at the potential of -0.6 V vs. SCE, while the highest value of 17.9 mA was reached at -1.2 V (SCE). When the electrodeposition time was 10 s (Fig. 6B), curves current vs. time had similar shape as the previous, but when the process duration prolongates to 60 s (Fig. 6C), currents obtained at higher potentials (-1.0 V and -1.2 V vs. SCE) decrease after about 15 s and stabilise again after about 40 s at some lower value (nearly 80% of the previous ones). Maximum theoretical thicknesses of Cu_2O film for every applied potential and all process durations were calculated. The lowest thickness of 7 nm was obtained for 6 s with potential of -0.6 V (SCE). More negative potentials and the increase of time lead to the increase of the film thickness. Theoretical value of the Cu_2O film thickness for the longest time (60 s) and most negative potential (-1.2 V vs. SCE) is about 900 nm.

3.2 Anodic oxidation

In spite of the simple equipment and easy process control, cathodic synthesis demands expensive chemicals as a big dissadventage. On the other hand, anodic oxidation of copper in alkaline solution is one of the standard methodologies for producing cuprous oxide powders used for marine paints and for plants preservation. Those powders are composed of particles of micrometer scale. However, solar sells, for their part, require particles or films of much smaller dimensions in order to achieve higher efficiency. Passive protecting layers formed on copper during anodic oxidation in alkaline solutions are widely investigated and described in electrochemical literature. The structure of those films formed on copper in neutral and alkaline solutions consists mainly of Cu_2O and CuO or $Cu(OH)_2$. Applying in situ electrochemical scanning tunneling microscopy (STM), Kunze et al. (2003) found that in NaOH solutions, a Cu_2O layer is formed at $E > 0.58-0.059$ pH (V vs. SHE). A $Cu_2O/Cu(OH)_2$ duplex film is found for $E > 0.78-0.059$ pH (V vs. SHE). In borate buffer solutions, oxidation to Cu_2O leads to non-crystalline grain like structure, while a crystalline and epitaxial Cu_2O layer has been observed in 0.1 M NaOH indicating a strong anion and/or pH effect on the crystallinity of the anodic oxide film.

Stanković et al. (1998; 1999) investigated the effect of different parameters such as temperature, pH and anodic current density on CuO powder preparation. The lowest value of average crystallite size was obtained at pH 7.5, whereas the highest value was obtained at pH 9.62. They found a strong dependence of grain size and cupric oxide purity on current density. The average srystallite size increased from 45 nm (at a current density of 500 Am^{-2}) to 400 nm (at a current density of 4000 Am^{-2}), other conditions being as follows: pH 7.5, temperature of 353 K and 1.5 M Na_2SO_4.

There have been a number of papers on anodic formation of thin Cu_2O layers (< 1 μm) using alkaline solutions, but some work has been done with slightly acidic solutions. For example, backwall Cu_2O/Cu photovoltaic cells have been prepared by Sears and Fortin (Sears & Fortin, 1983) with the Cu_2O layer being about 1 μm thick. They used and compared two methods of oxidation – thermal and anodic. The condition of the underlying copper surface is expected to influence the resulting parameters of thin solar cells, so they examined the influence of the surface preparation of the starting copper (i.e., polishing technique, thermal annealing). All this experience can help in researching the optimal way of production of nanostructured Cu_2O powders or films.

Recently, Singh et al. (2008) reported synthesis of nanostructured Cu_2O by anodic oxidation of copper through a simple electrolysis process employing plain water as electrolyte. They found two different types of Cu_2O nanostructures. One of them belonged to particles collected from the bottom of the electrolytic cell, while the other type was located on the copper anode itself. The Cu_2O structures collected from the bottom consist of nanowires (length, ~ 600–1000 nm and diameter, ~ 10–25 nm). It may be mentioned that the total length of Cu_2O nanothread and nanowire is comprised of several segments. These were presumably formed due to interaction between nanothreads/nanowires forming the network in which the Cu_2O nanothread/nanowire configuration finally appears. When the electrolysis conditions were maintained at 10 V for 1 h, the representative TEM microstructure revealed the presence of dense Cu_2O nanowire network (length, ~ 1000 nm, diameter, ~ 10–25 nm). The X-ray diffraction pattern obtained from these nanomaterials, could be indexed to a cubic system with lattice parameter, $a = 0.4269 \pm 0.005$ nm. These tally quite well with the lattice parameter of Cu_2O showing that the material formed under electrolysis conditions consists of cubic Cu_2O lattice structure.

In addition to the delaminated nanostructures, investigations of the copper anode, which were subjected to electrolysis runs, revealed the presence of another type of nanostructure of Cu_2O. Authors propose that the higher applied voltage (e.g. 8 V or 10 V) for electrolysis represents the optimum conditions for the formation of nanocubes. These nanocubes reflect the basic cubic unit cell of Cu_2O.

4. Conclusion

Copper oxides, especially cuprous oxide, are of interest because of their applications in solar cell technology. The semiconductor cuprous oxide Cu_2O film has been of considerable interest as a component of solar cells due to its band gap energy and high optical absorption coefficient. Since the properties of cuprous oxide not only depend upon the nature of the material but also upon the way they are synthesized, different methods and results obtained on the synthesis of cuprous oxide by various researchers are discussed in this chapter. The properties of the prepared cuprous oxide films related to surface morphology are presented too. In this chapter, the point is made on electrodeposition of cuprous oxide because electrodeposition techniques are particularly well suited for the deposition of metal oxides with thicknesses down to a few nm. The results obtained show that the cuprous oxide can be used as a potential active material for solar cells application.

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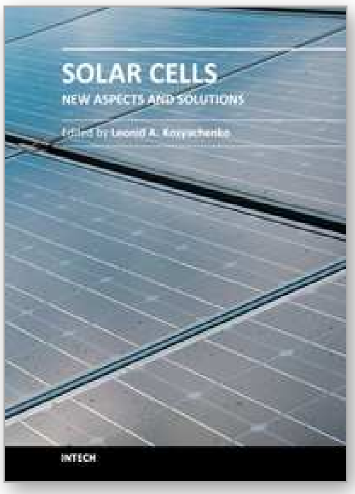

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The fourth book of the four-volume edition of 'Solar cells' consists chapters that are general in nature and not related specifically to the so-called photovoltaic generations, novel scientific ideas and technical solutions, which has not properly approved. General issues of the efficiency of solar cell and through hydrogen production in photoelectrochemical solar cell are discussed. Considerable attention is paid to the quantum-size effects in solar cells both in general and on specific examples of super-lattices, quantum dots, etc. New materials, such as cuprous oxide as an active material for solar cells, AlSb for use as an absorber layer in p-i-n junction solar cells, InGaAsN as a promising material for multi-junction tandem solar cells, InP in solar cells with MIS structures are discussed. Several chapters are devoted to the analysis of both status and perspective of organic photovoltaics such as polymer/fullerene solar cells, poly(p-phenylene-vinylene) derivatives, photovoltaic textiles, photovoltaic fibers, etc.

Sanja Bugarinović, Mirjana Rajčić-Vujasinović, Zoran Stević and Vesna Grekulović (2011). Cuprous Oxide as an Active Material for Solar Cells, Solar Cells - New Aspects and Solutions, Prof. Leonid A. Kosyachenko (Ed.), ISBN: 978-953-307-761-1, InTech, Available from: http://www.intechopen.com/books/solar-cells-new-aspects-and-solutions/cuprous-oxide-as-an-active-material-for-solar-cells

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