

# Deposition of Copper Oxide Thin Films by Chemical Techniques

By

Muhammad MUHIBBULLAH

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Department of Engineering Physics, Electronics and Mechanics,  
Graduate School of Engineering,  
Nagoya Institute of Technology,

Nagoya, JAPAN.

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## Abstract

Copper oxide (p-type) thin films were chemically deposited and characterized by compositional, structural, morphological, electrical, optical, photoelectrochemical and current-voltage (I-V) analyses and measurements. Both copper oxide ( $\text{Cu}_2\text{O}$  and  $\text{CuO}$ ) materials are advantageous for the photovoltaic application because their band gap, absorption coefficient and photosensitive properties are suitable for solar cells. Furthermore, they have low toxicity and good environmental acceptability, and the constituent elements are cheap and plentiful.

The  $\text{CuO}$  thin films were deposited on glass substrate by the chemical spray pyrolysis technique and their structural, electrical and optical properties were studied by XRD, Hall effect, and optical transmission measurements, respectively. X-ray diffraction data indicated that the deposited  $\text{CuO}$  was crystalline and had monoclinic crystal structure. Hall effect measurements showed that  $\text{CuO}$  was p-type with carrier concentration of about  $10^{15} \sim 10^{16} \text{ cm}^{-3}$ . The resistivity was low ( $30\text{--}90 \text{ }\Omega\text{-cm}$ ) and its value increased slightly with thickness but decreased with annealing. Thermoelectric power measurements showed a pinning of the Fermi levels at high temperature. The films were direct band gap semiconductors with an average band gap of 1.4 eV.

Copper oxide ( $\text{Cu}_x\text{O}$ ) thin films were deposited by the chemical bath deposition (CBD) technique.  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_3$  were used as the solution precursors with deionized water and the mixture was heated to  $\sim 80^\circ\text{C}$ . The film was deposited onto an indium tin oxide (ITO)-coated glass substrate. The substrate was immersed and placed horizontally at the bottom of the heated solution. The deposited films were crystalline with a cubic structure and had Cu/O ratios of 1.7–1.8. The oxygen contents were increased by bubbling oxygen gas into the solution during deposition. SEM images showed that the deposited samples were composed of octahedral particles. The particle size was little reduced and the shape was changed to more round one by the oxygen bubbling. Photo electrochemical measurement confirmed p-type and the photoconductivity of the films. In addition, the samples deposited with a few amount of ethylenediamine (EDA) added in the solution exhibited reduced-size octahedral particles, while the Cu/O ratio was increased to 2.

$\text{Cu}_x\text{O}$  thin films were deposited by the drop chemical deposition technique using the same concentrations of  $\text{CuSO}_4$  and  $\text{Na}_2\text{SO}_3$  as in the case of conventional CBD method. A small amount of the mixed solution was dropped onto the heated substrate. The deposited films were crystalline with a cubic structure of  $\text{Cu}_2\text{O}$  phase and had Cu/O ratio of  $\sim 1.3$  with very small amount of sulfur impurities. Surface morphology of the samples was relatively smooth without any cracks. In the optical transmission measurement, a clear absorption edge was observed near 800 nm wavelength. Photoelectrochemical measurements showed p-type and photoconductive films.

To fabricate the  $\text{Cu}_x\text{O}$ -ZnO heterojunction,  $\text{Cu}_x\text{O}$  layers were deposited by the CBD technique and the ZnO layer was deposited by electrochemical deposition. ITO coated glass sheet was used as the substrate. Both  $\text{ZnO}/\text{Cu}_2\text{O}/\text{ITO}$  and  $\text{Cu}_2\text{O}/\text{ZnO}/\text{ITO}$  heterostructures were fabricated and evaluated. Rectification properties and weak photovoltaic effects were observed. A solar conversion efficiency of 0.002% was obtained for the (write the type of structure here) heterojunction solar cells fabricated using the solution with EDA. The  $\text{Cu}_x\text{O}/\text{ZnO}$  heterojunction using  $\text{Cu}_x\text{O}$  layers deposited by the drop chemical deposition technique was also fabricated.

Rectification properties and weak photovoltaic effects were observed with an efficiency of 0.0012 %.

CBD, drop-CBD, and chemical spray pyrolysis techniques are considerably low-cost methods available for the deposition of  $\text{Cu}_x\text{O}$  and  $\text{CuO}$  thin films because they require inexpensive and simple apparatus. Hence, these chemical techniques are potentially suitable for the commercial production of low-cost solar cells.

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