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Junction and Material Properties of n-Cu_2O/p-CuI based Heterojunction Fabricated by Low-Cost Methods

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ABSTRACT

The photoelectronic industry has an enormous market in the world due to its ability to detect and utilize light based on different applications. Complex device fabrication methods and high production cost, associated with this processes and the materials, and the toxicity are few of the major drawbacks of the commercially available photodetectors in nowadays. Cu_2O and CuI are two of excellent wide bandgap photovoltaic semiconductor materials which can be fabricated using low cost method. Optoelectronic properties of an n-type cuprous oxide (Cu_2O) thin films prepared using a hydrothermal method and p-type cuprous iodide (CuI) thin film fabricated by drop cast method were characterized. The two films were identified as n-type and p-type respectively with carrier densities $\sim 2.2\times10^{19}$ cm^{-3} for Cu_2O and $\sim 8.6\times10^{17}$ cm^{-3} for CuI, respectively. Then the interfacial properties of a heterojunction, of the configuration ITO/Cu/n-Cu_2O/p-CuI/ITO were characterized with Bode plots, and Nyquist plots. The interface was identified to be a simple junction with parallel and series resister and capacitive properties.

Keywords: *Cu_2O, CuI, Heterojunction,p- and n-type semiconductors*

1. INTRODUCTION

The photoelectronic industry has an enormous market in the world due to its ability to detect and utilize light based on different applications. Up to now, light energy conversion plays a significant role in various types of energy harvesting and electronic based control systems[1]. Complex device fabrication methods and high production cost, associated with these processes and the materials, and the toxicity are few of the major drawbacks of the commercially available photodetectors in nowadays. Moreover, most of the photodetectors employ rare and toxic earth materials such as Indium (In), Germanium (Ge), Gallium (Ga), Cadmium (Cd), Sulfur (S) and Arsenic (As)[2]. Therefore, cost-effective broadband photodetectors using non-toxic materials are highly desired for efficient and environmental friendly photoelectric conversions.

Copper (Cu) is a non-toxic, environmental–friendly material, where the oxides of it (CuO and Cu_2O) have semiconducting properties. Therefore, CuO or Cu_2O based thin films optoelectronic devices are one of the alternative approaches to address this problem, and it has gained an extensive attraction of the scientific community due to the high efficiency, nontoxicity, high stability, and considerable lower manufacturing cost involved in Cu_2O and CuO. Among many metal oxide semiconductor materials, Cu_2O is considered as an excellent narrow bandgap photovoltaic semiconductor material with a bandgap of 2.0 eV[3]. *n-type* Cu_2O thin films can be prepared by various methods such as thermal oxidation, anodic oxidation, chemical deposition, sol–gel chemistry, sputtering, electrodeposition and other gas-phase deposition techniques[4].

When considering p-type semiconductors, the material reported by Satoshi Koyasu et al.[5], cuprous iodide (CuI) is also a semiconductor material which exhibits exciting features such as electrosensitivity, photosensitivity, and considerable bandgap energy (3.1 eV) [5]. This semiconductor has several potential applications in many areas including dye-sensitized solar cells as a hole conductor, as an effective reusable catalyst for various organic transformations and in light-emitting diodes due to its considerable exciton binding energy (62 meV)[6].
Satisfying the high demand for cost effective photodetectors, fabricated using simple device fabrication methods, is an essential requirements in the today's optoelectronic industry. As an effort, in this research work, results of optoelectronic characterization of a heterojunction device made with an n-type cuprous oxide (Cu_2O) thin film prepared using an atmospheric pressure hydrothermal method and a p-typecuprous iodide (CuI) thin film fabricated on the top of the Cu/n-Cu_2O photoelectrode by drop cast method which are inexpensive and straightforward techniques as compared to the conventional deposition techniques. Then the interfacial properties and opto-electronic properties of heterojunction were characterized and the structure, morphology and the properties of Junction resistance, Band alignment, and etc. were studied.

2. MATERIALS AND METHODS

2.1. Growth of Cu_2O and CuI layers

A piece of commercially available copper foil tape with conductive adhesive was used as the substrate, to grow the copper oxide thin film. An indium doped tin oxide (ITO) glass was used as the support to hold the copper strip and to facilitate the external electrical contacts, because with the ITO glass, an additional treatments on the Cu_2O film is not needed to make an electrical contact point. Prior to the Cu_2O film deposition, the ITO glass was cleaned with isopropanol and it was dried with an ambient air flow. Then copper tape was pasted on glass substrate. The glue layer on the ITO/Cu-tape interface do not affect the next step, the thin film growth, but a slight increase in the resistance at the interface is expected. The surface of the copper strip was cleaned with dilute nitric acid and washed thoroughly with distilled water. Then, the growth of the n-Cu_2O film on the copper-tapped ITO glass substrate was carried out by atmospheric pressure hydrothermal method using an aqueous 0.05 M $CuSO_4.5H_2O$boiled for 20-30 min while maintaining the temperature at 100°C. The copper-taped ITO glass substrate was kept in a vertical position, until a Cu_2O film with considerable film thickness was grown on the copper tape. The p-CuI layer was fabricated on top of the ITO/Cu/n-Cu_2O photoelectrode by drop cast method using a solution of CuI dissolved acetonitrile 0.01 M at 70°Ctill a sufficiently thin film of CuI was deposited.

2.2. Experimental techniques

Using prepared thin film heterojunction structures, a sandwich type cells were assembled as shown in Fig 1 to measure electrical parameters. The copper taped ITO glass was used as the lower contact. The upper electrode on the ITO/Cu/n-Cu_2O/ p-CuI structure was prepared by mounting a well cleaned ITO plate with a thin Pt layer sputtered on it. Finally, the ITO/Cu/n-Cu_2O/p-CuI/ITO-Pt layers properly fit together to obtain the sandwich type photodetector with an active area of 1 x 1 cm^2.

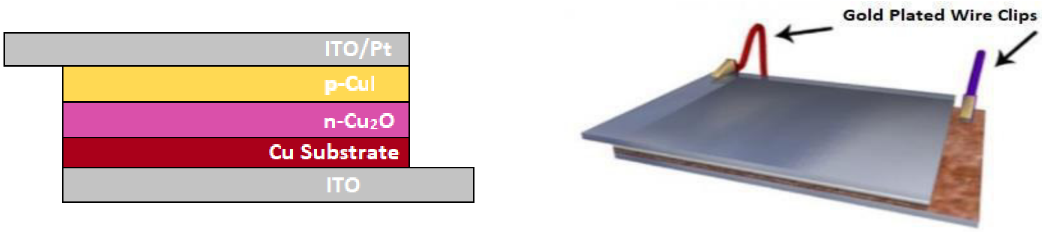
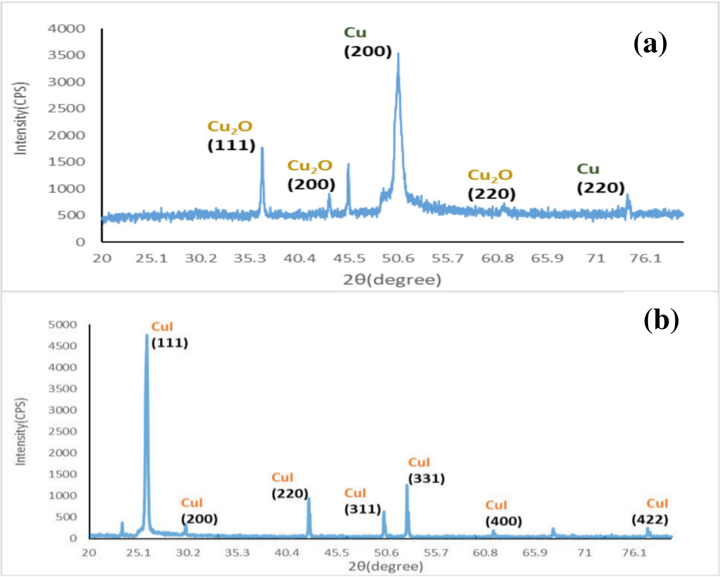


Figure 1: Theschematicdiagramof ITO/Cu/n-Cu_2O/p-CuI/ITO-Pt photodetector

X-ray diffraction (XRD) patterns, of individual materials and the embedded junction structure, were monitored using a RigakuUltima IVX-ray diffractometer. The XRD data were used to identify the phases present on the layer and their bulk crystal structures and any changes occur while the device fabrication process and aging.The Mott-Schottky plots were measured under dark by imposing a 10 kHz, 10 mV_{P-P} sine wave through a DC voltage sweep on to the photocathodes, while the DC potential was sweeping with a rate of 5 mVs^{-1}. For electrochemical impedance measurements, a 10 mV_{P-P} sine wave with varying frequency from 1 MHz to 0.1 Hz was imposed onto the cathodes under dark condition.The current-voltage measurement of n-Cu_2O/p-CuIthin films were measured in asolar simulator (CEP2000).For the IV characteristics under illumination, the devices were illuminated through the CuI side of the device through the ITO substrates, and the illuminated areas were 0.28 cm^2.

3. RESULTS AND DISCUSSION



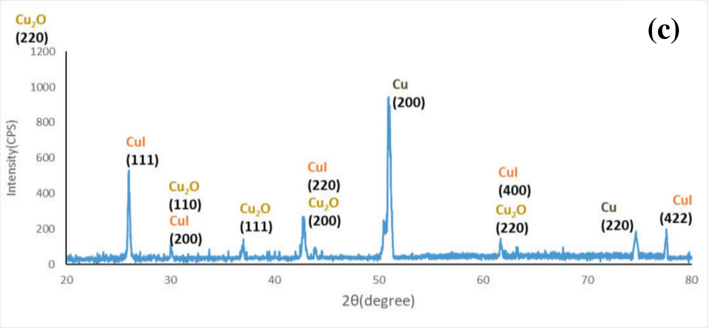


Figure 2. The XRD patterns of (a) Cu/n-Cu_2O film (b) p-CuI film, (c) Cu/n-Cu_2O/p-CuI film

The XRD spectrum of the Cu_2O films grown on the copper tape is shown in the Fig. 2.(a). Three different planes of Cu_2O, corresponding to the Cu_2O (111), Cu_2O (200) and Cu_2O (220) have been observed and identified through the XRD spectra. Two additional peaks were observed at 50° 18' and 74° 09'. The very intense peak at 50° 18' corresponds to the copper metal, the Cu (200) plane, and the peak at 74° 09' corresponds to Cu (220). Which has been resulted by the copper under layer or voids in the Cu_2O film, exposing the under layer.

Shown in the Figure 2.(b) is the XRD spectra of a thin film of CuI deposited on the ITO glass. The peaksobserved at 2θ values of 25° 16', 29° 53', 42° 29', 49° 78', 53° 46', 61° 33' and 76° 17' were from 111, 200, 220, 311, 331, 400 and 422 planes respectively.

Figure 2.(c) shows the XRD pattern of the Cu_2O/CuI electrodes on ITO substrate. ThecharacteristicpeaksduetoCu_2OandCuIappearon XRD pattern simultaneously. But some of these peaks are corresponding to the pure copper in the substrate. The XRD peaks at 36° 21', 42° 29' and 61° 33' were identified as the 111, 220 and 220 plane of Cu_2O as inthe Fig.2.(a), which are also matching with the values given in the literature for Cu_2O[7]. The very intense peak at 50° 18' corresponds to the copper metal, the Cu (200) plane, and the peak at 74° 09' corresponds to Cu (200). The XRD peaks corresponding to the CuI were observed at 25° 16', 29° 53', 42° 29', 61° 33' , 76° 17' and are identified as the corresponding peaks of the 111, 200, 220, 400 and 422 planes respectively. The sharp XRD peaks indicate that the Cu_2O and CuI are highly crystalline.

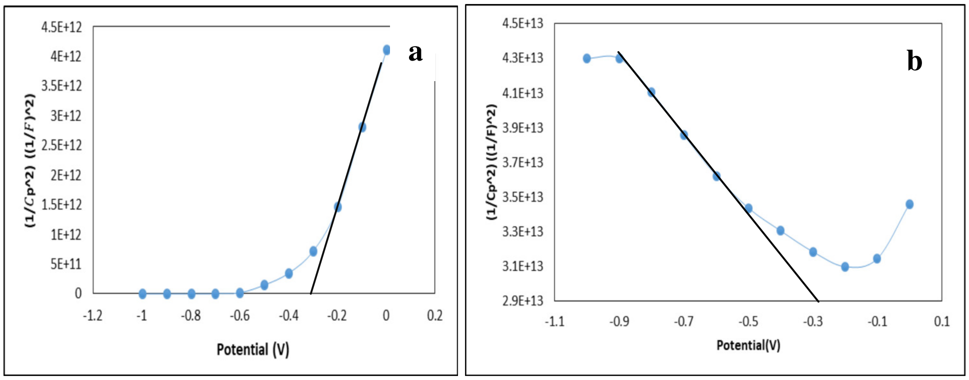


Figure 3. TheMott-Schottkyplotsof (a) Cu_2O and (b) CuI electrode from electrochemical impedance analysis in 0.5 M Na_2SO_4 aqueous solution.

The Mott-Schottky plot was used to estimate the majority charge carrier concentrations and the positions of the flatband potential (E_{fb}) of the semiconductor. Fig.3 shows the Mott-Schottky plots of the Cu_2O and CuI electrodes.This analysis is on a three electrode system with 0.1 M Na_2SO_4 as electrolyte, deposited copper oxide as theworking electrode, Pt wire as counter electrodeandAg/AgClinsaturatedNaClasreferenceelectrode. The positive slope in the Cu_2O plot (Fig. 3a) indicated that it is an n-type semiconductor and negative slope in the CuI plot (Fig 3b) indicated that it is an p-type semiconductor[8].For n/p-typesemiconductors,the majority carrier can be calculated using the following Mott-Schottky relationship[8],

$$\left(\frac{1}{C}\right)^2 = \frac{2}{eN_A\varepsilon_o\varepsilon_r A^2}\left(E - E_{fb} - \frac{KT}{e}\right)$$

WhereAisthesurfaceareaofthefilm,N_A isthe donor or acceptor density, ε_r is the dielectric constant of Cu_2O (6.6)[9]and CuI (8.4)[9], ε_o is the permittivity of free space, T is the temperature and k is the Boltzmann's constant.The carrier concentration calculated from slopes was $\approx 2.2\times10^{19}$ $cm^{-3}$for Cu_2O and $\approx$ 8.6×10^{17} $cm^{-3}$for CuI, respectively. The Mott-Schottky plot of theCu_2O electrode revealedtheflatband potential of the photocathode material to be, E_{fb}=−0.34 V vs RHE for Cu_2OandE_{fb} = -0.29 V vs RHE for CuI, respectively.

This observation confirms the n-type and p-type electrodes availability in the fabricated photodetector, which is helpful for effective separation of holes and electrons[10].

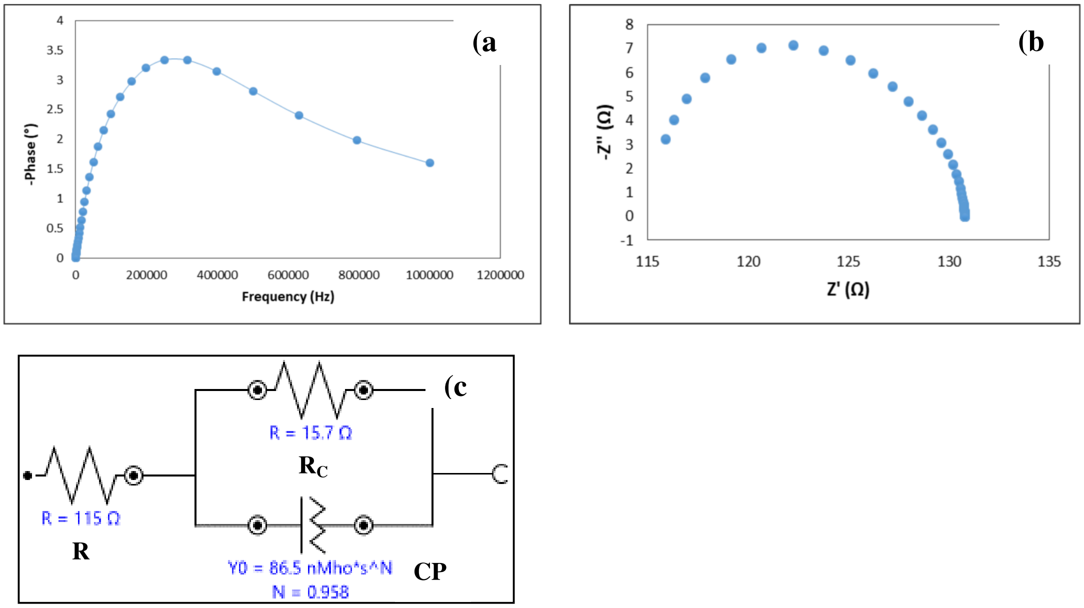


Figure 4. ElectrochemicalimpedancespectraofCu$_2$O/CuI photodetector: (a)Bodephase plots, (b)Nyquistplot, (c) The fitted equivalent electrical circuit of Cu_2O/CuI.

Electrochemical impedance spectroscopy (EIS) provides a powerful method for the study of charge transfer and hole-electron recombined processes and the internal resistance at the semiconductor interface [11]. Fig. 4(a) shows a typical EIS bode-phase plot obtained for Cu_2O/CuI. The peak frequencies of Cu_2O/CuI electrode is 25 kHz.The electron life time in the semiconductor can be calculated using following equation[11,12],

$$\tau_e = \frac{1}{2\pi f_{max}}$$

Where $\tau_e$is the electron lifetime, f_{max} is the frequency at the peak maxima in Bode Plots. The calculated electron lifetime for Cu_2O/CuI is 6.36 µs. The lifetime valuesgiveinsightintotherecombinationofchargecarrierswithinthe metaloxide.Carrier lifetime is strongly depended on the density of defects in the material which acted as recombination centers. Fig. 4(b) shows the Nyquist plotsmeasured under dark conditions in the frequency range of 10Hz to 1MHz for Cu_2O/CuI.The corresponding equivalent circuit is constructed and is shown in the Fig 4(c). In the equivalent circuit of Cu_2O/CuI correspond to one semicircle, the resistance R_S represents the series resistance of ITO and the contact resistance between the ITO and CuI;$R_{CT}$and CPE are the charge transfer resistance and constant phase element at Cu_2O/CuI interface.

4. CONCLUSION

Optoelectronic characterization were done for a n-type cuprous oxide (Cu_2O) thin films prepared using an hydrothermal method and a p-type cuprous iodide (CuI) thin film fabricated by drop cast method. The two films were identified as n-type and p-type respectively. The carrier densities of the respective films were estimate to be ~2.2×10^{19} $cm^{-3}$for Cu_2O and ~$8.6\times10^{17}cm^{-3}$ for CuI, respectively. The carrier density values are two to three ordered higher than expected values, but the polycrystalline nature of the films resulting in high density of defects may have resulted in these high values. The XRD spectra revealed the existence of different phases/planes of Cu_2O and CuI in the respective films, which confirms the polycrystalline nature of the respective thin films. Then the interfacial properties of heterojunction were characterized with Bode phase plots, and Nyquist plots. The interface was identified to be a simple junction with parallel and series resister and capasitive properties.

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Growing n-Cu_2O Thin Films on Transparent ITO Substrate to Replace the Opaque Copper Metal Substrate for Dye-Sensitized Solar Cells

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ABSTRACT

The world is facing the problem of fossil fuel shortage, and increasing crude oil prices. Hence, sustainable energies such as hydropower, wind power, geothermal power, solar power, and biomass are in the main focus in the energy research. The Dye-sensitized solar cells (DSSCs), classified as the third-generation photovoltaic offer a low-cost and nontoxic device, with functionalities such as flexibility and transparency. At present, titanium dioxide (TiO_2) is used as one of the electrode materials in DSSC. Among other different metal oxide materials, copper-base dioxide materials are of great interest in this context. To-date, most of the time, the Cu_2O working electrodes are fabricated on copper metal substrate. This only allows the devices to be back illuminated, which result in reducing the photo-response. Thus, the study presented here is focused on developing a nano-porous Cu_2O layer on a transparent substrate (ITO glass) with different methods, and study their optoelectronic properties in the aim of utilizing these electrodes in photovoltaic or opto-electronic device applications.

1. INTRODUCTION

Nowadays the whole world pays attention to the problem of fossil fuel shortage, and increasing crude oil prices. As a result, sustainable energies have been more focused in current fields in research. Hydropower, wind power, geothermal power, solar power, and biomass processing are few examples of the sustainable energies. Solar energy is one of the resources in archiving the target of a clean energy future. Everyday sun gives more energy ($\sim 1.73*10^{11}$ MW) than the need on the Earth ($\sim 1.73*10^{6}$MW)[1]. Solar panels convert this energy upon shining sunlight and convert them into electrical energy (electricity). There is no depletion in the incoming solar energy and this energy conversion process environmentally

The development of solar cell technology is been divided in to three generations. The first generation is the very costly single crystal silicon (Si) based solar cells, then the second generation is the low-cost thin film solar cell, but the materials used here are toxic and carcinogenic, and disposal of the devices are harmful for the environment. The Dye-sensitized solar cells (DSSCs) are classified as third-generation organic solar cells because they offer al low-cost and use anoxic materials in production. Additionally, they provide the functionalities such as flexibility and transparency, which are not offered by the first two generation devices [2]. Moreover, the ability that the DSSCs could be fabricated at low cost, in different colors, on a transparent glass or on flexible substrates have a huge potential in the commercial market, specially for "low-density" applications such as rooftop solar collectors and other small electronic gadgets. Another important feature is its operational hours at both ambient light and full sun condition without much impact on efficiency and also its ability to work at wider angles; when the other traditional solar cells would fail at illumination below a certain