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# Analysis of the ZnO/Cu<sub>2</sub>O and CdSe/Cu<sub>2</sub>O Thin Film Hetero-structure Electrode for Photo Electrochemical Solar Cell Applications

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# ABSTRACT

This paper proposes an economical route to the production of CdSe/Cu2O and ZnO/Cu<sub>2</sub>O based on commercial ZnO, CdSe corpuscle. The deposition of CdSe thin films was prepared by partial thermal oxidation method, Powder Vaporization method, and microwave oven method on the cleaned Cu<sub>2</sub>O substrate at room temperature. The solar cell fabrication process is greatly simplified by this method and opens a door in the direction of inexpensive techniques based on saleable available materials. The results show that the solar cell based on the mixture of CdSe/Cu<sub>2</sub>O has electron transportability, better light absorption, and high power conversion efficiency (PCE) of 0.7 was obtained. These materials have been characterized using FTIR, at which numerous peaks are present in the sample, and were assessed in detail. Multiple current-voltage characteristic curves were plotted, An open-circuit voltage VOC, a short circuit current  $I_{sc}$ , and the maximum power points Pmax were also noted. This work throws off more light in Enhancing the photoresponse of the electrode in both solar  $H_2$  generation and photoelectrochemical solar cell. **Key Words:** Photo Electrochemical, Thermal Oxidation, Chemical Etching.

# **1. INTRODUCTION**

In recent years, scientists and researchers demonstrate their interest in the direction of II-VI chalcogenide materials which get differ from the bulk material post doping scenario owing to the unique properties of thin films.[1-2] Due to its wide range of applications and interesting properties Cadmium selenide (Eg = 1.7 eV) is one of the binary semiconductors from II-VI group which has hypnotized attention of many researchers. Till date, scientific community explore different accepts of cadmium selenide (Cdse) nanostructure based thin films concerning to their basic properties and apply these properties for various applications like optical detectors, field effect transistors, dosimeters of ionized radiation, optoelectronic devices and solar cells. [3-4]. On the other hand, interstitial defects and natural vacancy in the ZnO crystal play a vital role in the electronic properties of the structure; reveal additional energy levels within the band gap, and change the junction efficiency [5–6].

P-type cuprous oxide (p-Cu<sub>2</sub>O) has long given attention by the researchers due to its remarkable theoretical conversion efficiency (approx. 20%) as a material for solar cells [7–8]. Moreover, this material has attracted immense attention for use in solar cells because it is suitable for building sustainable semiconductors, nontoxic and promising for cost-effective manufacturing [9–10]. Consequently, over the past few years the use of Cu<sub>2</sub>O for solar cells has been extensively studied.

Cuprous oxide (Cu<sub>2</sub>O) as a light-absorbing layer has attracted increasing attention in photovoltaic devices [11,12], due to its nontoxicity, copiousness [13], and electrical conversion theoretical efficiency of 20% for homojunction solar cell [20]. Cu<sub>2</sub>O films can be grown by several techniques including thermal oxidation [20–21], electrochemical deposition [18–19], chemical vapor deposition [17], magnetron sputtering [16] and pulsed laser deposition [15], among which the thermal oxidation method usually endue comparatively long minority carrier transport length and high crystalline quality, leading to higher power conversion efficiency (PCE). To date the highest PCE reported is 6.1% of the devices with Cu<sub>2</sub>O layer prepared by this method [20,22, 23].

However, high energy ingestion of this method curtail its application and high growing temperature (1000°C). Compared with thermal oxidation method, substitute method, e.g. electrodeposition method, offers several advantages like easy control of thickness and morphology, low cost, low deposition temperature, etc. [24,26]. A cuprous oxide with the band gap energy of about

2.09 eV is a native p-type semiconductor [27]. Due to the inability to obtain n-type  $Cu_2O$  for homojunction solar cell It is difficult to achieve a high efficiency for  $Cu_2O$ -based solar cell, [28, 29].

A well established method to grow high quality copper oxide, thanks to a thermal oxidation process from copper foils it is worth mentioning that the most efficient Cu<sub>2</sub>O photovoltaic devices were obtained. the high energy consumption of the thermal oxidation done under high temperatures (>1000 °C) for several hours, despite the excellent material properties of the resulting Cu<sub>2</sub>O, limits its application for a low cost industrial scale elaboration of solar devices. Several manufacturing processes using large area capable, environmental friendly and low cost methods are currently explored such as sputtering [30–31] or electrodeposition [32,33] In order to reach the photovoltaic market [30–31]. The spray pyrolysis process is among the high interest, low cost technologies, and the subject of increasing research for the production of Cu<sub>2</sub>O solar cells currently [34–35].

Cupric II oxide (CuO) and Cuprous I oxide (Cu<sub>2</sub>O) are the most studied transition metal oxides due to their interesting properties as a p-type semiconductor with band gap of about 1.2 and 2.2 eV, respectively [36, 37]. Cuprous oxide (Cu<sub>2</sub>O) is used as anode material in thin film lithium batteries [32] as well as in solar cells and is an attractive semiconductor material [39, 38, 40, 41].

Its semiconductor properties and the emergence of photovoltaic effect were discovered by Edmond Becquerel 1839th experimenting in the laboratory of his father, Antoine-César Becquerel. Cu<sub>2</sub>O is a p-type semiconductor with a direct band gap of 2.0–2.2 eV [42] which is suitable for photovoltaic conversion. Tang et al. (2005) found that the band gap of nanocrystalline Cu<sub>2</sub>O thin films is 2.06 eV, while Siripala et al. (1996)[43] 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.

 $Cu_2O$  its reasonably good electrical properties and attracts the most interest because of its high optical absorption coefficient in the visible range [43]. The unit cell of cuprous oxide 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 [44]. The oxygen O atoms in a bcc sublattice and the Cu atoms arrange in a fcc sublattice. The unit cell contains u 2 O atoms and 4 Cu atoms.

The aim of this present work is to prepare and fabricate photoelectrochemical solar cell of cadmium selenide and zinc oxide thin films as hetero-structure by a simple chemical vapour deposition and thermal oxidation to study the effect of hetero-structure based on the external solar cell parameters.

### 2.0 HYPOTHETICAL CONSIDERATION

The current is produced by injection from light, which make the solar cell to be seen as a current generator. The equivalent electrical model based on electrical components is been formed, to better investigate the electrical performance of solar cell.

The accomplishment of solar cells in space application is well acknowledged (e.g., communication satellites, unmanned and manned space exploration). Solar photovoltaic energy transition is used today for both space and terrestrial energy contemporaries. On globe are telephone communication, water pumping, transport etc. [35].

Nonetheless, the growing perceptive of the true price of fossil fuels with the necessitate for much more extensive use of solar cells in terrestrial applications is becoming clearer with the widespread require for renewable and environmentally satisfactory terrestrial energy resources.

This segment explicates the nature of the photovoltaic energy conversion principle entangled in the  $Cu-ZnO/Cu_2O/ZnO$  photoelectrochemical solar cells. The relevant solar cell current-voltage equation and those used for the computation of the fill-factor and the electrical power conversion efficiency of the fabricated solar cell are given.

Light is absorbed by a semiconductor immersed in an electrolyte solution in photoelectrochemical solar cells. At the semiconductor electrolyte interface charge separation takes place with the hole or electron stimulating an electron – transfer (redox) response at the surface. In Photo-electrochemical cells there are two primal types; photo electrolysis cells in which some of the light energy is used to drive a chemical reaction up hill in energy thus implementation as a type of solar battery and liquid – junction photovoltaic cells to convert light to electricity. The electron donors move the Fermi level ( $E_{F,SC}$ ) in n-type semiconductor toward the conduction band (see figure 1.0 below)



Fig 1.0: Schematic energy diagram in a photoelectrochemical solar cell

# 3.0 EXPERIMENTAL PROCEDURE

This part bring out the little by little procedure used in arriving at copper (I) oxide,  $Cu_2O$  starting from the initial element, Cu (copper). It also explicate how the Cu–ZnO/ $Cu_2O$ /ZnO and Cu–CdSe/ $Cu_2O$ /CdSe photoelectrochemical solar cell was constructed and the measurements of electrical power conversion efficiency, fill factor, open circuit voltage  $V_{oc}$  and the short circuit current  $I_{sc}$ . It also elucidate why the current-voltage characteristics measurement of the solar cell was measured.

For fabrication of  $Cu - ZnO/Cu_2O/ZnO$  photoelectrochemical solar cell it is essential for the p-Cu<sub>2</sub>O metal oxide semiconductor to be obtained first, the same thing with that of Cu–CdSe/Cu<sub>2</sub>O/CdSe. The process for obtaining this semiconductor and that for production of the photoelectrochemical solar cell is given below.

Firstly the Thermal oxidation method was conducted in a furnace, high purify copper (99.97%) in the form of foils (thickness 0.1mm) were cut into standard size wafers of  $2\text{cm} \times 2\text{cm}$ , The sample of copper foil were mantled up with tissue paper and smoothened by rubbing with the edge of a beaker to remove the kinks on the samples. The sample were cleaned by etching in dilute nitric acid, HNO<sub>3</sub> and rinsed in distilled water to remove any dross on the surface of the copper, and finally dried with oven at 40-50°C and stored in clean envelop ready for high temperature oxidation.

The oxidation temperature of 950°C was set after the furnace switched on. It took the furnace about one hour to attain the oxidation temperature and copper sample was placed in the ceramic crucible and place inside the furnace and oxidized for eight minutes (8mins) and instantly quenched in cold distilled water. The sample was removed from the distilled water and dried by placing them between tissue papers.

Secondly is the annealing of the sample, the oxidized samples were annealed at a temperature of 500°C. The annealed samples were quenched in cold distilled water and air dried.

Thirdly is Chemical etching process, Subsequent to cleaning of the sample, oxidation and annealing has been completed in addition to the liver red cuprous oxide (Cu<sub>2</sub>O) a black surface of cupric oxide (CuO) is usually formed. The black CuO was removed by chemical etching. Four (4) grammes of FeCl<sub>2</sub> and Four (4) grammes of NaCl were dissolved in 100ml of distilled water. 2ml of concentrated HCl was added to the solution, shaken carefully until the black colour is completely etched. The samples were then removed, rinsed with distilled water and dried between tissue papers and finally in air.

A further chemical etching was carried out using 8g of potassium persulphate dissolved in 100ml of the distilled water. The samples were as a final point rinsed in distilled water and dried between tissue papers. The appearing of characteristic liver red colour of  $Cu_2O$  considered the complete etching process.

The black CuO layer formed during oxidation was removed when shaken in a solution of  $FeCl_3$ , HCl and NaCl, leaving behind the red Cu<sub>2</sub>O.



Figure 2.0: Block diagram of the etching process

Fourthly After the chemical etching process the next method used in the synthesis of the sample is Chemical Vapour Transport, (CVT) (Figure 3.0) consists of mixing stoichiometric amounts of inorganic compound with the chalcogen, in this experiment we used the furnace oxygen as the chalcogen and Bromine (Br) as the transport agent in an unsealed vacuum. The unsealed vacuum was placed in-between the ceramic crucible and is then placed in a high-temperature furnace (700–1000°C), where a temperature gradient across the unsealed tube provides a driving force for the deposition of the CdSe and ZnO with the help of the transport agent (Br), forming ZnO/Cu<sub>2</sub>O/ZnO and CdSe/Cu<sub>2</sub>O/CdSe on both side of the sample Cu<sub>2</sub>O. Similarly another sample synthesized using microwave oven for 1 hour in order to study the photo response of the sample at 80°C with the help of the transport agent (Br) in a cylindrical container.



Fig 3.0: Chemical vapour transport

Lastly is cell fabrication 1 mole of NaCl (i.e the molecular mass dissolved in 1 liter of distilled water) was poured into the transparent plastic container. Copper wire electrodes were made to the synthesized  $ZnO/Cu_2O/ZnO$  and the copper counter electrode using silver paste and both placed inside the plastic container. A complete circuit was then made by connecting the two electrodes to a micro – ammeter as illustrated in fig 4.0.



Figure 4.0: Illustration of the fabricated ZnO/Cu<sub>2</sub>O/ZnO Photoelectrochemical solar cell.

# 4.0 RESULT AND DISCUSSION

The efficiency, maximum power, photo voltage and photocurrent was obtained under illumination (Table 1.0), and the Cu-ZnO/Cu<sub>2</sub>O/ZnO Pec solar cell showed characteristic curves with short-circuit current and open-circuit voltage followed by conversion power efficiency. When tested in the Hadejia Jigawa State Nigeria, The calculated external parameters of the manufactured sample Cu- ZnO/Cu<sub>2</sub>O/ZnO are stated in table 1.0. Three different readings are recorded using a multimeter and numerous solar irradiances in order to study the solar cell parameters, three dissimilar graphs are studying for the same sample for testing photo response of the electrode under illumination, table 2.0 is for the synthesized Cu- CdSe/Cu<sub>2</sub>O/CdSe the deposited CdSe increase the photo response at the same time increasing the efficiency of the sample, where under solar light irradiation it works as an absorber to generate charge carriers (electrons and holes). The first two rows in table 2.0 is for CdSe using thermal oxidation method while the last row is for CdSe layer deposited using microwave oven.

# Table 1.0: The photo voltage, efficiency, maximum power, and photocurrent of different readings of Cu- ZnO/Cu<sub>2</sub>O/ZnO photoelectrochemical solar cell

S/N	I <sub>SC</sub>	V <sub>oc</sub>	P <sub>MAX</sub>	η
1	13.74mA	6.30mV	$8.56 \times 10^{-5} W$	0.6%
2	18.00mA	178mV	$216.66 \times 10^{-5} W$	0.1%
3	18µA	110mV	$318.75 \times 10^{-5} W$	$7.0  imes 10^{-4}\%$

# Table 2.0: The photo voltage, efficiency, maximum power, and photocurrent of different readings of Cu- CdSe/Cu<sub>2</sub>O/ CdSe photoelectrochemical solar cell

S/N	I <sub>SC</sub>	V <sub>oc</sub>	<b>P</b> <sub>MAX</sub>	η
1	3.50mA	33.2mV	$262.3 \times 10^{-5} W$	0.7%
2	222mA	84mV	81.2× 10 <sup>-5</sup> W	0.2%
3	10.40mA	101.1 mV	113.9× 10 <sup>-5</sup> W	0.4%



Figure 5.0: Is the graph of Fourier transform infrared (FTIR) spectroscopy of synthesized CdSe/Cu<sub>2</sub>O/CdSe



Figure 6.0: Is the graph of Fourier transform infrared (FTIR) spectroscopy of synthesized CdSe/Cu<sub>2</sub>O/CdSe



Figure 7.0: Is the graph of Fourier transform infrared (FTIR) spectroscopy of synthesized ZnO/Cu<sub>2</sub>O/ ZnO in microwave oven

Figure 7.0 shows the analysis of ZnO/Cu<sub>2</sub>O/ZnO FTIR. The results can be concluded as follows: There are more than five peaks, regarding the number of peaks, designating that the analyzed chemical is not a simple chemical but rather a complex molecule. The peaks compromised single bond area (2500-4000 cm<sup>-1</sup>). A hydrogen bond is noticeable at broad absorption band in the range of between 3650 and 3250 cm<sup>-1</sup>. While for hydroxyl compound it also has been confirm due the presence of spectra at frequencies of 1600–1300, 1200–1000 and 800–600 cm<sup>-1</sup>. The existence of oxygen-related bonding was present due to the presence of sharp bond at about 3500 cm<sup>-1</sup>. There is no aromatic structure found due to no appearance of a peaks between 3000 and 3200 cm<sup>-1</sup>. On account of narrow bond absent at less than 3000 cm<sup>-1</sup> responded to there is no C-C bond. In between 2700 and 2800 cm<sup>-1</sup> no specific peak for aldehyde has been found. There is triple bond region (2000-2500 cm<sup>-1</sup>) was perceived, informing there is C=Cbond in the material. Regarding the double bond region (1500-2000cm<sup>-1</sup>), there is no huge and sharp peak was detected informing that there is no double bond. This informs that there is no carbonyl double bond, from ketones, aldehydes, esters, or carboxyl. No peak at about 1600 cm<sup>-1</sup>, demonstrating that there is no C=C bonding in the sample. Based on above interpretation, several conclusions can be obtained, including the analyzed material has hydrate component. This sample has no ketones-related component, there is triple bond in the material. Since the peaks were only about 10 peaks, the material should be a small organic compound. The absorbance seen below 1500 cm<sup>-1</sup> is the fingerprint frequencies, these are highly characteristic of the molecule as a whole; they tell what is going on surrounded by the molecule, as well in this infrared spectrum region however some functional groups will absorb. In addition to all mention above Figure 6.0 On account of narrow bond present at less than 3000 cm <sup>1</sup>responded to C-C bond due to synthesis in microwave oven for one hour, Figure 5.0 There is no triple bond region (2000-2500  $cm^{-1}$ ) was perceived, informing that there is no C=C bond in the material.

# **5. CONCLUSION**

In summary, we fabricated a Cu<sub>2</sub>O based hetero-structure solar cell with a ZnO and CdSe film as the buffer layer. The electrical and structural properties of ZnO/Cu<sub>2</sub>O/ZnO&CdSe /Cu<sub>2</sub>O/CdSe films under different solar irradiance were investigated. Manufacture of Cu<sub>2</sub>O thin films at 950°C using partial thermal oxidation was successful and the deposition of inorganic compound at 700°C in a high temperature furnace with help of driving force as a result of the temperature gradient within the surrounding of the unsealed tube. In order to understand the mechanism of synthesized sample FTIR characterization and Photocurrent measurements demonstrated the successful deposition of cuprous oxide from the initial material copper foil and I-V characteristic showed typical rectification behavior of a *p*-*n* junction for the fabricated structure, indicating that ZnO/Cu<sub>2</sub>O/ZnO was formed as a semiconducting material and utilizing carbon dross photovoltaic effect is a hopeful way for high photo response of the CdSe sample which lead to PCE of 0.7%. The fabricated cell produced a power conversion efficiency of 0.7%, 0.6% and 0.4% respectively using numerous method.

#### **Authors Contributions**

M. Abdurrahman reviewed the literature, designed the methodology, restructured the article, extract the data and make it meaningful information, produced all figures, interpretation of the results, F.W Burari and O.W Olasoji supervised the entire work.

#### **Conflict of Interests**

The author(s) have not declared any conflict of interests.

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