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Fabrication of Schottky Barrier Solar Cells of Copper (I) Oxide (Cu_2O) by the Process of Partial Thermal Oxidation

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Abstract: Copper (1) Oxide (Cu_2O) is a non-stoichiometric semi-conductor. It is envisaged that this semiconductor could be used for the fabrication of low-cost solar cells. These solar cells have been fabricated by researchers using 100 micrometer thick copper sheets. For the purpose of this research, copper foil sample was oxidized in air between 250^0C and 1050^0C. The oxide films grown were then investigated by means of SEM. This research produced Cu/Cu_2O solar cells with copper sheet 100 micrometer thick using prolonged annealing times and different annealing temperatures to study the development that were achieved in solar cell performance. The investigation of morphology was taken by scanning electron microscopy and (I – V) curve have been carried out, a cell of 42mV open-circuit, voltage, V_{oc}, 6.7 µ A. short circuit current, I_{sc} and conversion efficiency of 1.42X10 -4% has been achieved .in this research also detected the effect of prolonged annealing time on the performance of Cu/Cu_2O Schotkky barrier solar cell due to continuous reaction of cuprous oxide with oxygen.

Keywords: Copper (1) Oxide (Cu_2O), non-stoichiometric, semi-conductor

INTRODUCTION

Semiconductor thin film technology has drawn much attention for research due to its excellent properties and applications in optoelectronics devices, solar cells, sensors and laser materials. The process of thin film deposition has rapidly developed since its discovery, especially its application as a solar cell material.

The electrical and optical properties or Cu_2O, depending on deposition condition such as solution PH, solute concentration deposition potential and temperature were investigated by [1] and found out that the solution PH controls the flat band voltage, which determines the conduction type of Cu_2O. Flat band voltage of the Cu_2O increases positively as the PH of the deposition solution increases. He also found that the band gap of Cu_2O is not sensitive to the deposition conditions such as solution PH and deposition voltage.

Musa *et al*. carried out a research on the thermal oxidation process using XRD & SEM studies and found out that the oxide layers that resulted from oxidation at 1050oc were basically of Cu_2O, and those that were grown below 1040oc were mixed oxides of Cu_2O and CuO. He also observed that the lower the temperature of oxidation, the lower the amount of Cu_2O present in the oxide. This research further suggested that the annealing process results in dense polycrystalline Cu_2O layers of increased grain sizes that are appropriate for solar cell fabrication [2].

Tang *et al*. carried out a research on the electro chemical deposition of nanocrystallineCu2O thin films on TiO2 films coated on transparent conducting oxide (TCO) glass substrates by cathodic reduction of cupric acetate (O.1m sodium acetate and 0.02m cupric acetate). The authors found out that the PH and bath temperature strongly affect the composition and microstructure of the Cu_2O thin films. They also investigated the effect of bath PH on electro-deposition of Cu_2O thin film by selecting a bath temperature of 30oc and an applied potential of -245mV Supercritical Carbon (iv) oxide Emulsions (SCE). The authors found that the films deposited at PH 4 are mostly metallic Cu and only little Cu_2O. In the region of PH4 to PH5.5, 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 [3].

Using three different substances i.e. stainless steel, platinum and copper, Bugarinovic *et al*. carried out an investigation on the electrochemical deposition of thin films of cuprous oxide at room temperature. Electrode-position was carried out in a copper lactate solution as an organic electrolyte. The authors found that the composition of the substrate strongly affects the electrochemical reactions. They found out that reaction with the highest rate occurred on the copper surface and the reaction with the lowest rate occurred in the platinum electrode. It was concluded that the co-deposit or Cu_2O and Cu was obtained at -800mV (SCE) on stainless steel electrode [4].

EXPERIMENTAL PROCEDURE

In order to prepare a clean and good Cu2O the characteristics of the original copper surface was considered. Before oxidation, industrial-grade copper sheets of 0.01mm thickness and 99.95% purity was cleaned in 35% nitric acid for about 30s to wipe away impurities. And it was cut into regular sizes of 6cm by 3cm. It was then thoroughly washed in distilled water and dried using tissue paper.

THERMAL OXIDATION

The oxidation was carried out at atmospheric pressure in a vector rectangular furnace. A ceramic crucible was used to hold the samples. When the oxidation temperature was reached, the samples were carefully put inside the furnace.

The temperature and time of oxidation were varied for both complete and partial thermal oxidation of the samples. Some specimens were then oxidized in the presence of HCl vapour. A flow of Ar gas at a pressure of 5×10^{-5} Nm^{-2} from a high pressure cylinder transported the HCl vapour to the samples during oxidation

ANNEALING AND QUENCHING

After the oxidation, the samples were quickly quenched in distilled water. The furnace temperature reduced to 600^0C and the samples were then given a second heat treatment (annealing) for 120 min, and followed by a second quenching. Black CuO were formed on the surface of the Cu_2O

CHEMICAL ETCHING

After the process of quenching in distilled water and for all oxidations that were carried out below 1000oC. Selective etching to remove CuO was performed using: a solution consisting of 5g of FeCl3, 20cm3 of HCl, and 8MHNO3 containing NaCl for 3mins. The last stage of the etching process was carried out using a solution of potassium persulphate in water.

ELECTRICAL MEASUREMENTS AND SEM ANALYSIS

The conductivity type of the oxides was obtained by means of the hot-probe thermoelectric method. The collinear four-point probe method, the van der Pauw and Hall measurements were used to measure the resistivity and mobility of samples.

The surface morphology and microstructure of the specimens were analyzed using a Hitachi 52400 SEM

CURRENT-VOLTAGE (I-V) CHARACTERISTIC MEASUREMENTS

The I - V characteristic measurement was carried out on the back - wall Schottky barrier solarcells that was fabricated both in the dark and under illumination.

The characteristic in the dark was used to measure the solar cell parameters like, the dark saturated current density, Jo and the solar cell series and and shunt resistances.

The characteristic under illumination was used to measure the open - circuit voltage,Voc, the short circuit current density, Jsc, the maximum power point for the fabricated solar cells, Pmax and finally, the electrical power conversion efficiency of the solar cells.

RESULTS AND DISCUSSION

Fig (1) is the SEM micrograph showing surface morphology of a copper foil partially oxidized at 1050^oC for 3 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 of the formed $CuO/Cu_2O/Cu/Cu_2O/CuO$. The hot-probe thermoelectric measurement confirms a P-type CuO. Roos et al. measured a band gap of 1.5 eV for CuO [5] in his work reported registering a higher open-circuit voltage (V_{oc}) for CuO/Cu_2O heterojunction solar cells compared to frontwall Cu/Cu_2O solar cells and concluded that these cells appear to belong to a basically different class of cells [6] also suggested the use of CuO/Cu as a solar thermal selective absorber.

Fig: 2 and Fig 3 show the SEM micrograph of the morphology and crystallinity of annealed CuO surfaces oxidised at $1050^{o}C$ for 3 min. after the etching process, respectively. At this temperature there is recrystallization and normal grain growth in the material resulting in equiaxial of Cu_2O. There are gaps observed between the grains, wich could be as a result of incomplete grain growth after the oxidation process. The gaps are areas full of dislocations and vacancies. Fig 2 shows an appreciable compactness and considerable growth of the grains. The disappearance of the gaps between the crystal grain as seen in Fig 3 is as a result of crystal growth which occurred during the annealing process. The average grain size for the crystals of the un annealed Cu_2O sample in Fig 3 was estimated to be $0.66\mu m$. in addition to normal grain growth in this material, there is the annihilation of crystal defects such as vacancies and dislocations.

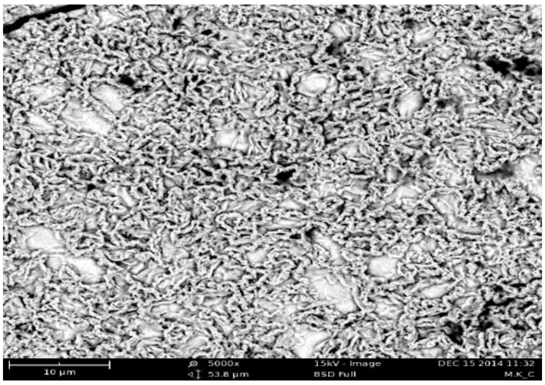


Fig-1: SEM micrograph of unetched and unannealed sample oxidised $1050^{o}C$ for 3 min. showing CuO coating.

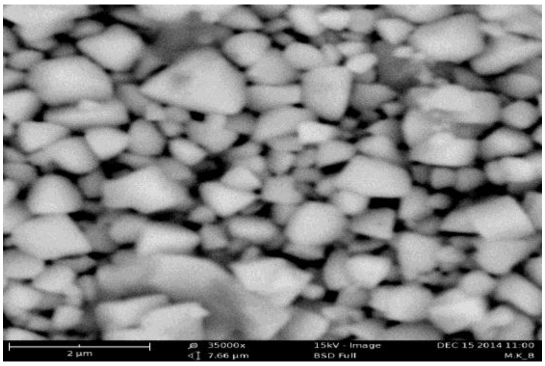


Fig-2: SEM micrograph of sample oxidised at 1050OC for 3 min. and annealed at 500OC for 90 min after etching

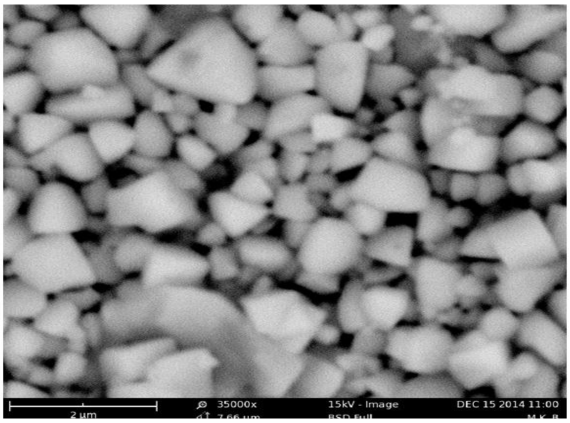
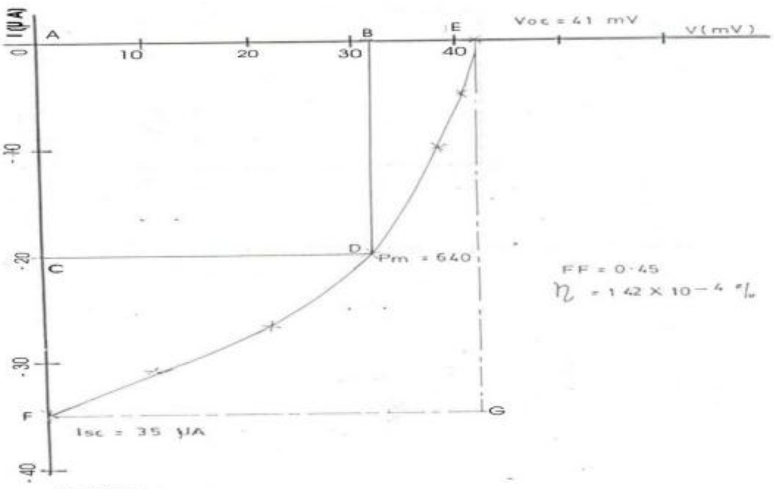
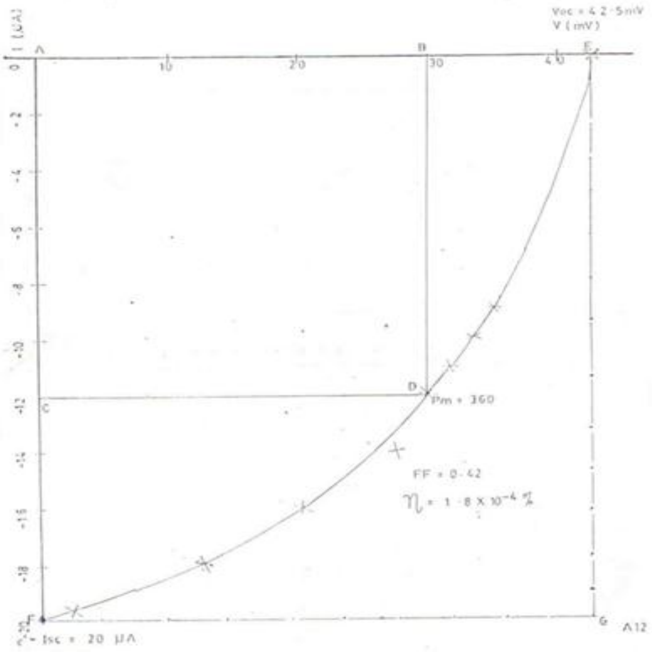


Fig-3: SEM micrograph of sample oxidised at 1050oC for 3 min. but unannealed after etching

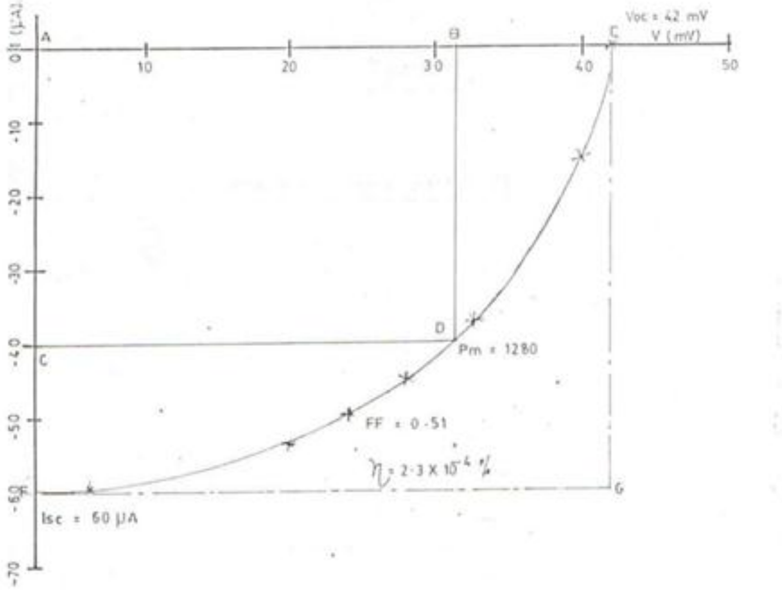


Graph A I-V CHARACTERISTICS UNDER ILLUMINATION



Graph B

I-V CHARACTERISTICS UNDER ILLUMINATIOBN



Graph C

I-V CHARACTERISTICS UNDER ILLUMINATION

DISCUSSIONS

OXIDATION PROCESS

The samples which initially had rough surfaces before dipping them in solution of $Fecl_2$, Hcl and NaCl became smooth and bright after it were dipped in the solution.

The samples were immediately quenched in cold distilled water as it was brought out of the furnace to disallow further oxidation in air. Folding was observed in samples brought out of the furnace and left to cool down in air instead of quenching in cold distilled water due to compressive stress. Annealing at 500°C was performed to:

- Reduce defects created during the high temperature oxidation.
- Reduce the resistivity of copper (I) oxide and to.
- Improve on the crystallinity of the copper (I) oxide.

The copper foils were oxidized at various temperatures and times. From the results obtained, it was observed that samples oxidized at temperature above 1050°C composed entirely of Cu_2O. After the oxidation and annealing processes, black substances were observed on the samples, showing the presence of copper (II) oxide (CuO). Copper (II) oxide is also a photovoltaic material. Its band gap of 1.5eV is actually at optimum [7]. The hot-probe method has been used to confirm a P-type conductivity for CuO [5]. Higher open-circuit voltage V_{oc} for CuO/Cu_2O heterojuction solar cell were observed [5] when compared to frontwall Cu/Cu_2O solar cells, the authors concluded that these cells appeared to belong to a basically different class of cell.

After etching the samples, the reddish brown-colour of Cu_2O became visible. This result shows that the aim of the oxidation process was achieved since it is the copper (I) oxide that is required for the fabrication of the backwall solar cells.

It was observed that temperature and time played important roles in the oxidation process. The higher the oxidation temperature, the more the copper (I) oxide layer deposited on copper. However, irrespective of the oxidation temperature after the annealing process, copper (II) oxide is always formed. It was also observed that copper foils oxidized at a very high temperature for a long time became fragile break into small pieces during the etching process.

This showed that the oxidation of the samples required high temperature and relatively short period of time (3 minutes) for thermal oxidation.

Copper (I) oxide has been identified to be stable only at limited ranges of pressure, the stable oxide is copper (I) oxide. During thermal oxidation, copper (I) oxide is formed first after sufficiently long oxidation time, copper (II) oxide is formed [8].

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