

Effect of Annealing on the Structural and Photovoltaic Properties of Cadmium Sulphide: Copper Sulphide (CdS:Cu_xS) Heterojunction

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Abstract- The effect of annealing on the structural, optical and the photovoltaic properties of CdS:Cu_xS heterojunction formed by acid etching of sintered CdS layer prepared and dipping it into a cuprous ion solution were investigated for the purpose of fabricating cheap and high efficient solar cell. Each of the CdS:Cu_xS sample prepared was characterized using the X-ray diffractometer (XRD), UV-visible spectroscopy and the I-V measurement in dark and light condition after annealing at 200 °C, 250 °C and 300 °C. The study concluded that annealing was crucial for optimizing structural and optical properties of CdS:Cu_xS heterojunction which eventually affect the photovoltaic properties of the samples.

Index Terms- Thin films; heterojunction, sintered CdS, Photovoltaic, x-ray diffractometer

I. INTRODUCTION

CdS:Cu₂S heterojunction is one of the promising candidates for fabrication of low cost solar cells. CdS:Cu₂S solar cell is clearly heterojunction cell with CdS having energy gap of 2.41eV [2] and Cu₂S having a direct energy gap of 1.21 eV [1]. However, fabricating cheap, high efficient and large area solar CdS:Cu₂S heterojunction solar cell remains a difficult scientific and technological problem.

Early studies related to Cu₂S/CdS heterojunction solar cells generally involved Cu₂S/CdS heterojunction solar cells fabricated by a variety of techniques including a combination of spray pyrolysis/wet dipping [3, 13], evaporation/wet dipping [6], all-sputtering [14, 15], all-evaporation [1, 4, 7] and sputtering/evaporation [11]. Each of the above listed techniques has some advantages and disadvantages. A cost/quality ratio may serve as an important criterion of selection.

More so, annealing is one of the basic technological processes used for reducing stress on deposited films, to improve mismatch, formation of new phases and point defects and to achieve interdiffusion between elements through an interface. Annealing can activate Cu diffusion into CdS layer producing Cu_xS phase and Cu-doped CdS layer.

In this work the cheapest method of fabricating CdS:Cu_xS solar cell has been employed using sintering/wet dipping method and the effect of annealing on the structural, optical, and photovoltaic characteristics of the solar cells have been investigated.

II. MATERIALS AND METHODS

Commercially available cadmium sulphide (CdS) powder and 10%wt cadmium chloride (CdCl₂) were thoroughly mixed with few drops of ethylene glycol to form slurry solution as reported in literature [12] The solution thus prepared was printed on both soda lime glass substrates and indium Tin Oxide (ITO) coated substrates which had been cleaned by washing with detergent, rinsed with distill water, rinsed with acetone, methanol, isopropanol and dried in vacuum oven. The films thus prepared were dried at 100°C for 2 h in air atmosphere. The reason for drying the sample at lower temperature was to avoid cracks and to minimize pin hole in the samples. The CdS films were then sintered at 400 °C for 30 minutes in the air atmosphere. The temperature of the furnace was allowed to cool before removing the CdS film from the furnace.

To obtain the Cu_xS absorber layer, the sintered CdS films prepared were etched with 10% HCl, rinsed with deionized water held at 90°C before immersed in hot (90°C) saturated CuCl solution for few seconds, rinsed with warm deionized water and dried. Each of the CdS:Cu_xS sample was then annealed at temperature 200 °C, 250 °C and 300 °C for 15 minutes in relatively vacuum environment. A very thin layer of Cu_xS was then formed on the top surface of CdS thin film as a result of Cu diffusion following the reaction:



Finally to complete the photovoltaic structures, a layer of conducting silver was printed over the ITO/CdS/Cu_xS films. The samples prepared were analyzed using mini MD 10 X-ray diffractometer, Jenway 6504 uv-visible spectrophotometer, Keithley 2400 source meter coupled with a Newport solar simulator for structural, optical and photovoltaic properties respectively.

III. RESULTS AND DISCUSSION

(A) Structural Characterization

X-ray diffractometer (MD 10 X-ray mini) was employed to obtain X-ray diffractograms of CdS sintered films and the Cu_xS:CdS thin film at room temperature. These diffractograms were analysed to obtain crystallographic properties of these samples. The copper target was used as a source of CuK α radiation with wavelength of 1.54178 Å. The scanning angle (2 θ)

was in the range of 15 °–75 °. The presence of sharp and well defined structural peaks in XRD patterns shown in figure 1, confirmed the polycrystalline nature of the CdS sintered films. The XRD pattern showed no peaks of CdS oxidation. The diffraction peaks at $2\theta = 24.96^\circ, 28.25^\circ, 37.14^\circ, 43.61^\circ, 47.63^\circ$ and 51.48° can be indexed to hexagonal (wurtzite) structure of CdS according to JCPDS (card number 06-0314). The lattice parameters, 'a' and 'c' were calculated using the relation [12]

$$\frac{1}{d} = \frac{4}{3} \left[\frac{h^2 + hk + l^2}{a^2} \right] + \frac{l^2}{c^2} \quad (2)$$

where d is the inter planar spacing, determined using Bragg's equation and h, k, l are the Miller indices of the lattice

planes. The evaluated lattice parameters for the CdS sintered film are $a = 4.144 \text{ \AA}$ and $c = 6.602 \text{ \AA}$.

Similarly, figure 2 shows the XRD pattern of CdS:Cu_xS thin films annealed at 200, 250 and 300 °C. It was observed that the peaks are sharp and well defined indicating that the samples are polycrystalline in nature. The Prominent diffraction peaks at $2\theta = 27.51^\circ, 30.93^\circ, 41.32^\circ$ and 50.03° corresponds to diffraction angle of 102 plane of Cu_{1.96}S, 200 plane of Cu₂S, 106 plane of Cu₂S and 200 plane of CdS respectively. The mixed phase of Cu_{1.96}S and Cu₂S was in agreement with what was reported in the literature [9]. This result, also suggested that as the annealing temperature increases the rate of diffusion of Cu to the CdS layer increases.

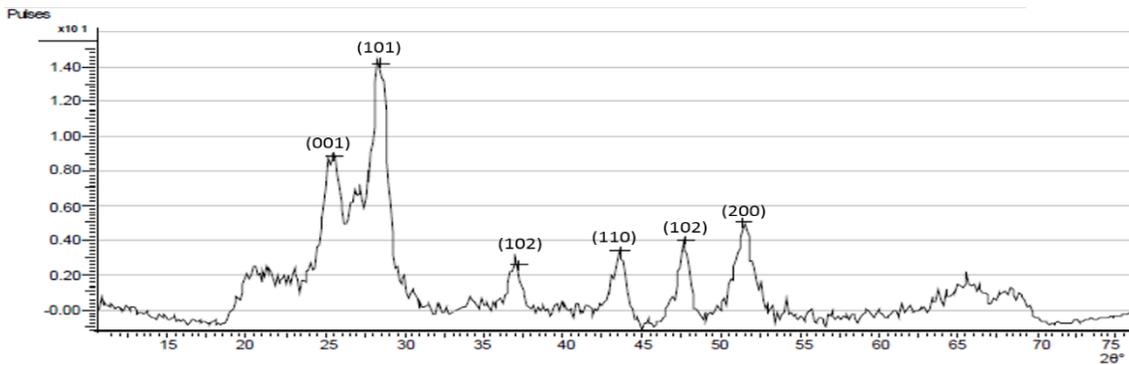


Figure 1: The XRD Pattern of Prepared Sintered CdS film

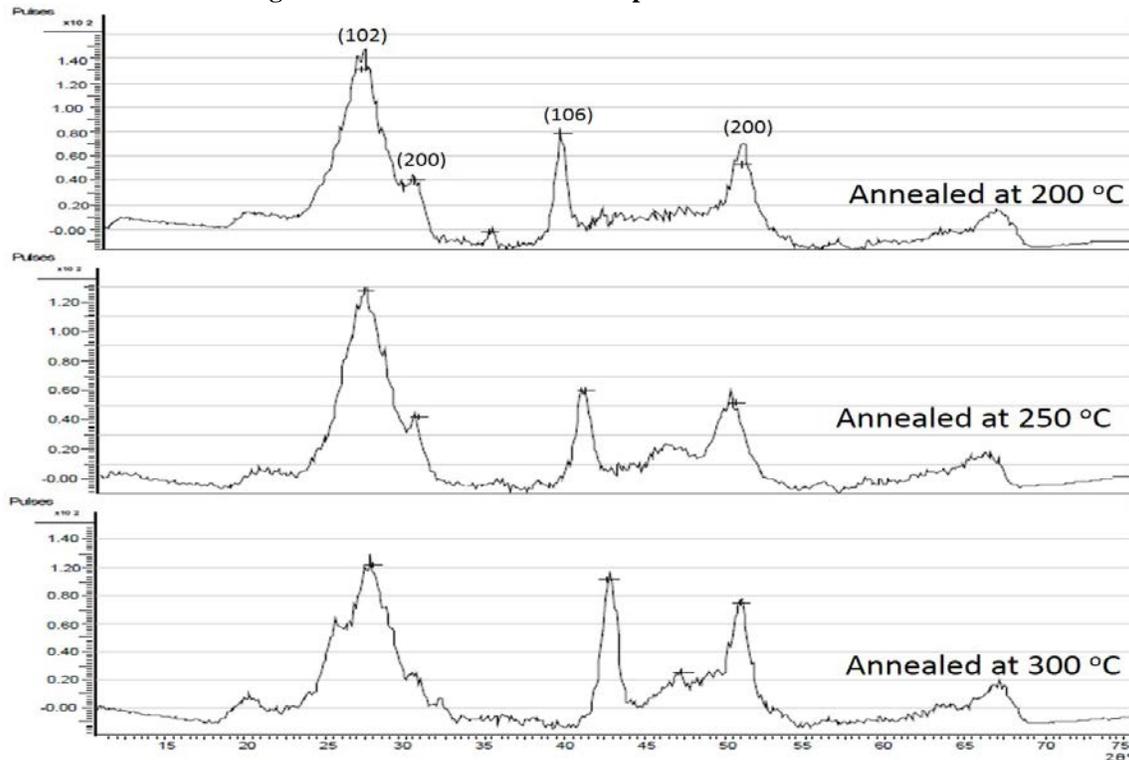


Figure 2: The XRD Pattern of Prepared CdS:Cu_xS thin film

(B) Optical Characterization

The optical transmittance spectral of samples were measured in the wavelength range 200 to 1150 nm using the 6504 Jenway uv-visible spectrophotometer. The readings obtained were utilized to compute the absorption coefficient α given by;

$$\alpha = \frac{1}{t} \ln \left(\frac{1}{T} \right) \tag{3}$$

where t is the thickness of the film and T is the transmittance.

The optical band gap was also determined using the Tauc relationship which is given by the formula [8]

$$\alpha h\nu = A (h\nu - E_g)^n \tag{4}$$

where $h\nu$ is the photon energy and E_g is the band gap and A is the constant which is different for different transitions and $n = 1/2$ for direct band gap material.

The optical transmission spectra for sintered CdS in figure 3(a) indicate that the CdS film possessed high transmission in the visible region of the spectrum. Also, the absorption coefficient was estimated and found to be high, of the order of 10^4 cm^{-1} . For determination the energy band gap, a graph of α^2 versus E (eV) is plotted as shown in Figure 3(b). The extrapolation of straight line to $\alpha^2 = 0$ axis gives the value of the energy band gap of CdS film to be 2.38 eV within an accuracy of ± 0.02 eV. This optical data analysis for CdS film indicates that direct allowed transitions occur in these films that is the maximum of valence band and the minimum of conduction band lie at the same value of electron wave vector k in $E - k$ band diagram and hence the transitions are of direct type. This result is in agreement with the value reported in other studies [2, 8]. The wide band gap and high optical absorption coefficient of CdS sintered films will be an added advantage in respect of their applications in photovoltaic devices.

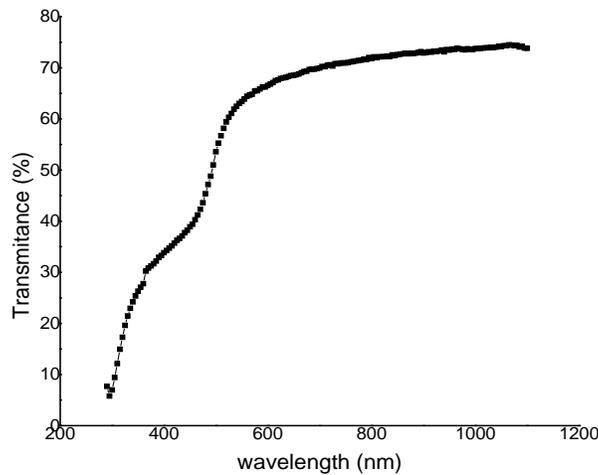


Figure 3(a): Optical Transmittance versus wavelength of sintered CdS thin film

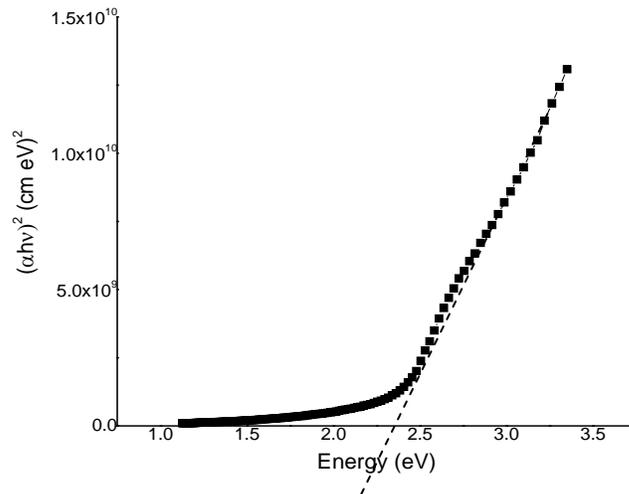


Figure 3 (b): Absorption Coefficient Square $(\alpha h\nu)^2$ of Sintered CdS film

(C) I-V Characterization

The current-Voltage (I-V) characteristics of the solar cell structure in dark and under illumination were measured using the Keithley 2400 source meter controlled with a computer interface using Labview software. The dc voltage was source from 0 to +400 mV. The I-V characteristics was used to demonstrate the some of the photovoltaic properties of the samples. The I-V characteristic without illumination (in dark), for cell annealed at 200°C, 250°C, and 300°C is shown in figure 4(a). The cells have rectifying properties; the I-V plots were similar to diode characteristics and the current increases as the annealing temperature increases.

However figure 5(b) shows the I-V characteristic plots of the solar cell annealed at 200 °C, 250 °C and 300 °C respectively under illumination intensity of 50 mW/cm². The solar cell parameters such as I_{sc} (V=0), V_{oc} (I=0) and fill factors (FF) were calculated using the following equations

$$FF = \frac{V_{max} I_{max}}{V_{oc} I_{sc}} \quad (5)$$

$$\eta = \frac{P_{max}}{P_{in}} = \frac{FF (V_{oc} I_{sc})}{P_{in}} \quad (6)$$

From the results shown table 4(b) it can be stated that as the annealing temperature increases, the V_{oc} increases from 230 – 439 mV while, the I_{sc} decreases from 281 – 235 uA as the annealing temperature increases from 200 °C to 300 °C decrease. However, the Fill Factor and the conversion efficiency increases as the annealing temperature from 200 °C to 250 °C but, at 300 °C the fill factor and efficiency decreases. Annealing at 300 °C or more degrades the cells. This could be the consequence of the diffusion of copper into the CdS bulk resulting in the deficiency of copper in the Copper Sulphide layer.

Table 1. Evaluated I_{sc}, V_{oc} and fill factor (FF)

Sample	I _{sc} , (μA)	V _{oc} (mV)	Fill factor
Annealed at 200°C	6.86	235	0.413
Annealed at 250°C	6.08	248	0.500
Annealed at 300°C	5.63	291	0.356

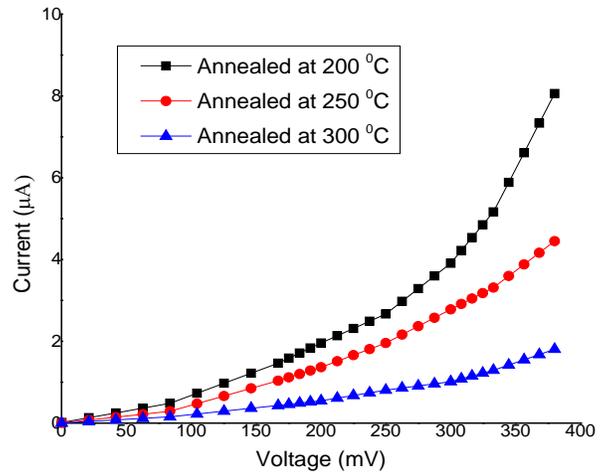


Figure 4 (a): Dark I-V Characteristics of prepared CdS:Cu_xS Thin film

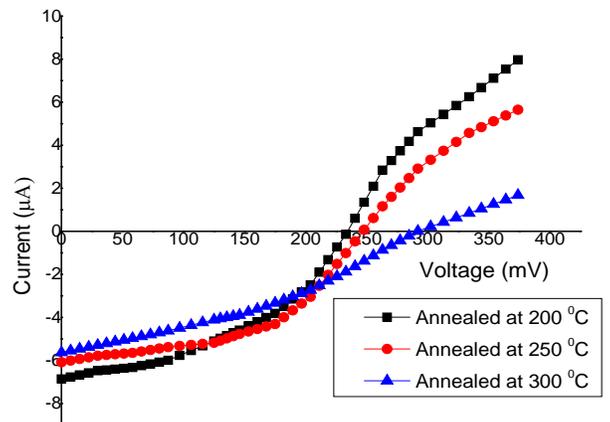


Figure 4 (b): I-V Characteristics under illumination (50mW/cm²) of prepared CdS:Cu_xS Thin film

IV. CONCLUSION

Using a combination of characterization techniques such as XRD, UV-visible spectroscopy and the I-V characteristics, detailed information of the effect of annealing on the structural, optical and the photovoltaic properties of CdS:Cu_xS heterojunction solar cell prepared by sintering, and wet dip methods were obtain.

The prepare CdS:Cu_xS film samples annealed at 200 °C, 250 °C and 300 °C exhibit the mixed phase of Cu_{1.96}S, Cu₂S,Cu and CdS which is due to the diffusion of Cu to the interface of the CdS layer. The optical spectra of the Cu_xS layer show that the samples possessed high transmission in the near IR region and

high absorption in the visible region of the spectrum. The analysis of the spectra shows that the samples have energy band gap ranging from 1.19 - 1.17eV. The energy band gap of the Cu_xS decreases as the annealing temperature increase from 200 to 300 °C. The shift in the energy band gap is due to the change in the compositional structure of the films as a result of increase in annealing temperature.

It can also be concluded from the I-V characteristic analysis that, increase in annealing temperature caused the V_{oc} to increase and the I_{sc} to decrease. However, the fill factor increase as the annealing temperature increases from 200 to 250 °C but, at the temperature of 300 °C the fill factor decreases for both film. This could be the consequence of the diffusion of copper into the CdS bulk resulting in the deficiency of copper in the Copper Sulphide layer.

It is therefore inferred that annealing is crucial for optimizing structural, and optical properties of CdS: Cu_xS heterojunction which eventually affect the photovoltaic properties of the solar cell fabricated.

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