

# TEMPERATURE DEPENDENT CHARGE TRANSPORTATION AND RECOMBINATION MECHANISM IN $\text{Cu}_2\text{S}/\text{CdS}$ HJT SOLAR CELL

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## ABSTRACT

A heterojunction solar cell has been fabricated by chemical method by using green synthesized  $\text{Cu}_2\text{S}$  (p-type) and  $\text{CdS}$  (n-type) nanostructures. Thin films of Copper Sulfide ( $\text{Cu}_2\text{S}$ ) and Cadmium Sulfide ( $\text{CdS}$ ) were deposited on Indium tin oxide (ITO) coated glass substrate by chemical bath deposition (CBD) method. Silver (Ag) and ITO used as back and front electrodes during current-voltage (J-V) characterization. Silver was fabricated by vacuum coating method. The photovoltaic properties of the fabricated device were recorded for 300K, 310K, 320K, 330K and 340K respectively. The short circuit current density ( $J_{sc}$ ), open circuit voltage ( $V_{oc}$ ), fill factor (FF) and efficiency ( $\eta$ ) were calculated for the heterojunction at different temperatures. There was no antireflecting coating during the J-V characterization of the cell. The efficiencies of the device were gradually increased from 300K to 320K then decreasing for higher temperature. Green synthesized  $\text{Cu}_2\text{S}/\text{CdS}$  heterojunction solar cell can have maximum efficiency of 1.68% at 320K without any antireflecting coating.

**Keywords:** CBD method, Heterojunction, Solar Cell, Temperature, Efficiency.

## I. INTRODUCTION

Thin film occupies a prominent place in basic science research and device fabrication technology. The use of thin film semiconductor has attracted much interest in an expanding variety of applications in various electric and optoelectronic devices due to low production cost [1-3]. In the field of photovoltaic, the recent investigations are directed towards the development of cost effective and nontoxic environmental friendly materials that can be synthesized by a simple method for fabrication of solar cell. A heterojunction is formed by joining two layers of semiconductors with different band gap energies [4-7]. Nanostructures of  $\text{Cu}_2\text{S}$  and  $\text{CdS}$  have been studied extensively because of excellent photovoltaic properties [8, 9]. The present work has been focused on the fabrication of heterojunction solar cell with green synthesized  $\text{Cu}_2\text{S}$  (p-type) and  $\text{CdS}$  (n-type) nanostructures.

Various efforts have been made by the workers for fabrication of  $\text{Cu}_2\text{S}/\text{CdS}$  heterojunction by using different methods. Yue Wu et al. presented a radial synthesis of colloidal copper sulfide ( $\text{Cu}_2\text{S}$ ) nanocrystals and demonstrated their application as an active light absorbing material in combination with  $\text{CdS}$  nanorods to fabricate a heterojunction solar cell. They reported highest efficiency of 1.6% for the cell and stability over four

month testing period. The work explained a low temperature solution-phase process for deposition of thin films [10].

T Potlong et al. made the heterojunction of n-type CdS and p-type CdTe for solar cell fabrication. The depositions of different layers were carried out by closed space sublimation (CSS) and high vacuum evaporation (HVE) method. They used CdTe (1.5 eV) as p-type light absorbing layer and CdS (2.42 eV) as higher band gap n-type material. They allowed the passing of sunlight through a transparent contact and CdS was acting as a window layer of the device. They explained the CdS/CdTe heterojunction as a low cost solar cell with higher efficiency [11]. Again K Anuar et al. used cathodic electro deposition in presence of EDTA in aqueous solution for preparation of Cu<sub>2</sub>S film on Ti substrate. They found that the optimum deposition potential for the preparation of Cu<sub>2</sub>S is -0.40V and higher concentrations of CuSO<sub>4</sub> to a fixed concentration of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> was with better photo activity. The energy band gap of prepared Cu<sub>2</sub>S film was 1.5 eV [12]. The efficiency of a simple heterojunction structure for Cu<sub>2</sub>S/CdS solar cell based on chemical method has been investigated at different temperatures in this present work.

## II. EXPERIMENTAL

For the fabrication of heterojunction solar cell, thin films CdS and Cu<sub>2</sub>S nanostructures were used as n-type and p-type layer in the junction. The nanostructures were prepared by chemical method. Cadmium Acetate solution of 0.1 M concentration was prepared in starch solution (3% by volume in distilled water) with constant stirring at room temperature. The pH of the solution was maintained at 9 by adding ammonia solution. Then sodium sulfide (Na<sub>2</sub>S) solutions of 0.1M concentration were added to the reaction bath in continuous supply of nitrogen gas. The mixtures were stirred for another 2 hour for the growth of CdS nanostructures. The detailed synthesis procedure was explained by R.Saikia et al. in their previous work [13]. Again nanostructures of Copper sulfide were synthesized by using chemical route using starch as capping agent. Cupric Acetate solutions were prepared at 0.1 M concentration by using starch matrix and adding ammonia solution for keeping pH at 9. Finally Cu<sub>2</sub>S was synthesized by adding sodium sulfide solution to the Cupric Acetate solution and stirred for 2 hours in presence of nitrogen gas. The green growth of Cu<sub>2</sub>S nanostructure was reported R.Saikia et al. in their earlier works [14]. Cleaning of substrate is very important for solar cell performance. Long diffusion length of minority carriers are necessary for high efficiency cell and required low levels of metal contamination at the substrate before high temperature treatment. The conventional cleaning of substrate consists of two steps. The first step consisting of an NH<sub>4</sub>OH/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture, aims at organic particle removal whereas in the second step a HCL/H<sub>2</sub>O<sub>2</sub>/H<sub>2</sub>O mixture is used to remove the metal contaminants. As a transparent conductive material, indium tin oxide (ITO) has been utilized as front electrode for fabrication of solar cell. The ITO coated glasses were purchased from sigma Aldrich. The thickness of ITO film was 500 nm, resistivity of  $4 \times 10^{-4} \rho.cm$  and transmittance was about 95%. A thin film of CdS nanostructures was first formed on ITO coated glass by CBD method after cleaning the substrates and then a thin layer of Cu<sub>2</sub>S was deposited on CdS layer. This chemical bath deposition is simple and cost effective method for deposition of CdS and Cu<sub>2</sub>S films. Again silver (99.99% pure) was deposited as back electrode by vacuum evaporation method under high vacuum of  $10^{-6}$  Pa [15,16]. The fabricated device was heated at 450 K temperature for 10 minutes in air for junction formation and also to improve the efficiencies [17]. The thickness of CdS and Cu<sub>2</sub>S layers were measured by AFM as 100 nm and 3

μm respectively. The schematic cross sectional diagram of the cell in the configuration of glass/ITO/CdS/Cu<sub>2</sub>S/Ag with surface area of about 1 cm<sup>2</sup> is shown in Fig.1.

### III. RESULTS AND DISCUSSIONS

CdS and Cu<sub>2</sub>S nanostructures are well known n-type and p-type material for solar cell fabrication. The nanostructures of CdS and Cu<sub>2</sub>S were prepared by chemical method. The structural and optical properties of the thin films were studied by HRTEM, SAED and UV-Vis analysis respectively. The particle sizes were obtained from HR-TEM analysis. The average size of CdS nanorods were calculated as 8 nm to 10 nm from HR-TEM measurement as shown in Fig.2. On the other hand, the average sizes of Cu<sub>2</sub>S nanostructures were measured as 5 nm to 14 nm in Fig.3. The high crystallinity with continuous lattice fringes throughout the nanostructures were revealed by selected area diffraction (SAED) pattern. The diffraction rings in Fig.4 could be indexed to (110), (311) lattice planes of hexagonal CdS [JCPDS file no. 6-314] and (220) for cubic CdS [JCPDS file no. 10-454] nanostructures. Again in Fig.5 (101) [JCPDS file no. 47-1748] and (102), (103) [JCPDS file no. 26-1116] planes were assigned for hexagonal Cu<sub>2</sub>S along with a ring of hexagonal CuS nanostructures for plane (110) [JCPDS file no. 06-0464]. The absorption corresponding to electron excitation from the valence band to conduction band can be used to determine the nature and value of optical band gap of the material. The absorption spectra for both of the samples have been recorded in the range of 100 nm to 800 nm as shown in Fig.6. The absorption peak of CdS was found at 319.0 nm from Fig.6 (curve a) and energy band gap estimated for it was 3.89 eV. Cadmium sulfide is used as wide energy band gap n-type material. The nanostructures of Cu<sub>2</sub>S have potential photovoltaic application as active light absorbing p-type layer due to higher absorption coefficient as a low energy band gap material. A representative UV-Vis spectrum of Cu<sub>2</sub>S nanostructure shown a wide absorption up to 800 nm with a peak centered at 695.0 nm in Fig.6 (curve b). The calculated value of energy band gap was 1.78 eV.

There was no antireflection coating in the current density-voltage measurement of the cell. Representative current density (J)-voltage (V) characteristics recorded on the as made photovoltaic device shown a typical reflection behavior under zero illumination (dark current) at 300K temperature in the Fig.7. The applied potential was in the forward bias direction. The dark current curve was showing the turn-on and built-up of the forward bias current in the diode. Without illumination, no current flows through the diode unless an external potential was applied. Under a standard illumination of irradiance 100 mW/cm<sup>2</sup>, A.M= 1.5G at 300K, the device revealed the solar cell characteristics. With incident sunlight, the shifting of J-V curve identified the external current flow from the solar cell. The short circuit current density J<sub>sc</sub>, flows with zero external resistance and the maximum current was delivered by solar cell at any illumination level. Again, the open circuit voltage V<sub>oc</sub>, was the potential developed across the terminals of the solar when the external load resistance is very large. The current- voltage curve of a solar cell yields an important operational parameter called the fill factor or FF is given as

$$FF = P_{max} / V_{oc} I_{sc} = V_{mp} I_{mp} / V_{oc} I_{sc} = V_{mp} I_{mp} / V_{oc} J_{sc} \dots \dots \dots (1)$$

Actually the fill factor does not depend on the area of the device. One can increase the voltage by adding more cells in series and one can increase the current by wiring more cells in parallel. The solar conversion efficiency is given by

$$\eta = (FF \cdot V_{oc} \cdot J_{sc}) / P_s \dots\dots\dots(2)$$

Here  $P_s$  is the input solar irradiance. In this case  $P_s = 100 \text{ mW/cm}^2$  for 1.5 G. This quantity can be best measured with broadband pyranometer. The J-V characteristic of the cell at 300K was recorded by Keithley electrometer as in the Fig.7. The cell exhibits the short circuit current density  $J_{sc} = 4.5 \text{ mA/cm}^2$ , the open circuit voltage  $V_{oc} = 0.57 \text{ volt}$  and fill factor is about 0.57. Efficiency of the fabricated solar cell was calculated as 1.46%. In Fig.8, J-V characteristics were done at temperatures varying from 300K to 340K respectively. Open circuit voltage  $V_{oc}$  was decreasing from 0.57 to 0.50 for temperature range 300K to 320K whereas it was again increasing from 330K to 340K as shown in Table 1.

**Table 1: Voc, Jsc, FF and efficiency ( $\eta$ ) of the heterojunction at different temperatures.**

Temperature (K)	$V_{oc}$ (V)	$J_{sc}$ (mA/cm <sup>2</sup> )	FF	$\eta$ %
300	0.57	4.5	0.57	1.46
310	0.55	4.7	0.60	1.55
320	0.50	5.2	0.65	1.68
330	0.51	5.1	0.64	1.66
340	0.52	4.8	0.65	1.62

Similar change of short circuit current density was observed with variation in temperature. The cell efficiency was increasing from 1.46% to 1.68% for temperatures 300K to 320K and then decreasing for temperature 330K and onwards. The maximum efficiency was recorded for 320K temperature and was about 1.68%. The detailed values of  $J_{sc}$ ,  $V_{oc}$ , FF and efficiency ( $\eta$ ) are reported in Table1. Therefore significant variations of efficiencies were observed over the entire temperature range from 300K to 340K temperatures. The J-V characteristics have shown that the fabricated device pronounced decrease in performance, at higher temperature. All characterizations were carried out for total cell surface area of  $1 \times 1 \text{ cm}^2$ . The major reason for decreasing the efficiency of a heterojunction solar cell is may be due to the fact that each photon irrespective of its high energy generates electron hole pairs. These electrons and holes are quickly thermalised at higher temperatures. The energy thus wasted and is dissipated as heat. Excessive recombination of electrons and holes in the semiconductor nanostructures at higher temperature at the surface of the junction also reduces the cell efficiencies.

**IV. CONCLUSIONS**

Heterojunction structure of CdS/Cu<sub>2</sub>S was fabricated by sequential chemical bath deposition method. Required sizes of nanostructures were synthesized by chemical route by using starch as capping agent. With many semiconductors were available the chemical deposition method but the present green synthesized nanostructures offers promises for future work. Cadmium sulfide (CdS) and copper sulfide (Cu<sub>2</sub>S) nanostructures were used as n-type and p-type layers in the formation of solar cell. Indium tin oxide (ITO) and silver (Ag) were used as front and back electrodes for current voltage characterization of the cell. Thin films were deposited by CBD method on ITO coated glass whereas

silver (Ag) was deposited by vacuum coating method. The sizes of CdS and Cu<sub>2</sub>S nanostructures were calculated from HRTEM analysis. The average sizes of CdS nanorods were 8 nm to 10 nm whereas Cu<sub>2</sub>S nanostructures were measured as 5 nm to 14 nm. The crystalline nature of the nanostructures was revealed by HRTEM SAED pattern. The energy band gap for CdS was calculated as 3.89 eV and that of Cu<sub>2</sub>S was 1.78 eV. The Cu<sub>2</sub>S nanostructures were used as p-type light absorbing material. The current voltage characterizations were carried out without any antireflecting coating. The maximum efficiency of the cell was reported as 1.68% at 320K temperature. The open circuit voltage Voc, short circuit current density Jsc and fill factor (FF) were estimated as 0.50 V, 5.2 mA/cm<sup>2</sup> and 0.65 at 320K temperature. The efficiency of the cell was decreasing for higher temperature than that of 320K. It may be due to thermalisation of electrons and holes of the heterojunction at higher temperature. The performance of the solar cell can be improved by using antireflecting coating and texturing the front or back surface of the device.

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## Figure Legends

Fig 1: Structure of CdS/Cu<sub>2</sub>S heterojunction solar cell.

Fig 2: HRTEM image of CdS Nanostructures

Fig 3: HRTEM image of Cu<sub>2</sub>S Nanostructures

Fig 4: SEAD image of CdS Nanostructure

Fig 5 : SEAD image of Cu<sub>2</sub>S Nanostructure

Fig 6 : UV-Vis Spectra of CdS and Cu<sub>2</sub>S nanostructures

Fig 7 : J-V characterization of the cell at 300K temperature

Fig 8 : J-V characterization of the cell at different temperatures

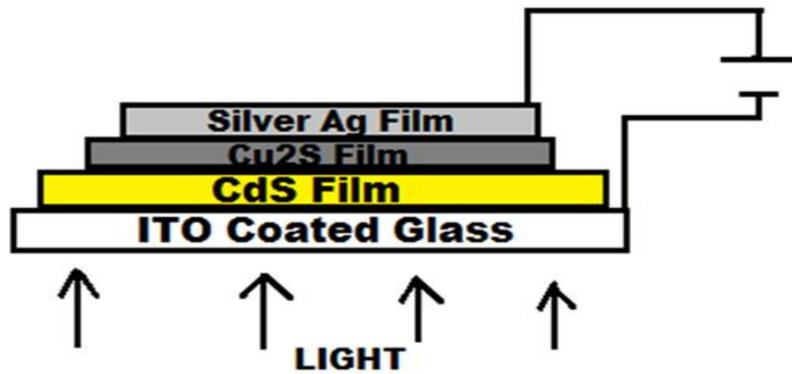


Fig 1

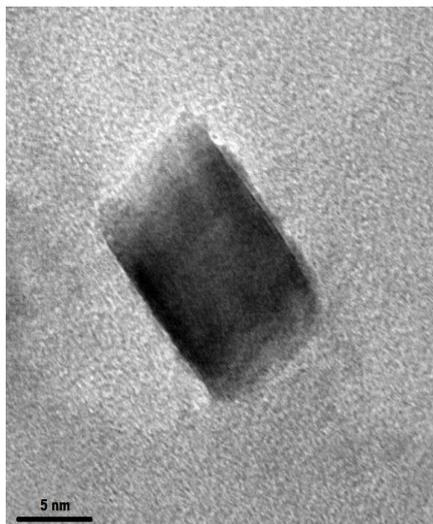


Fig 2

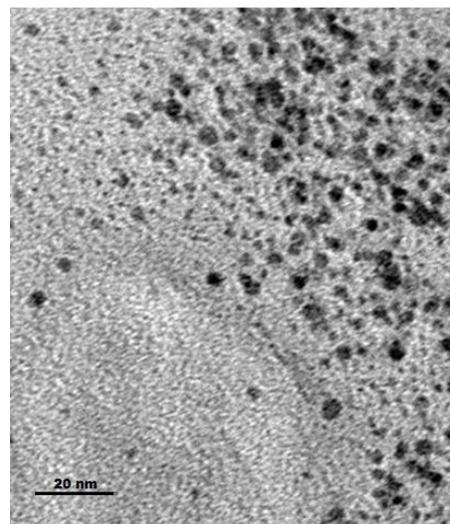


Fig 3

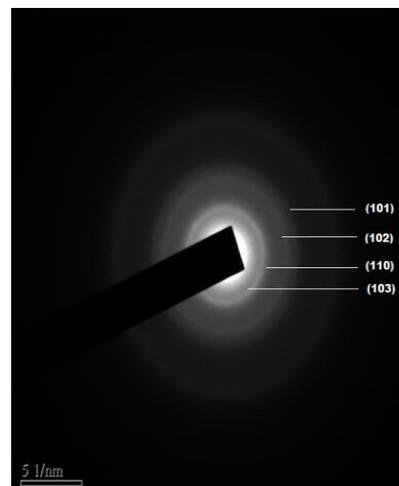
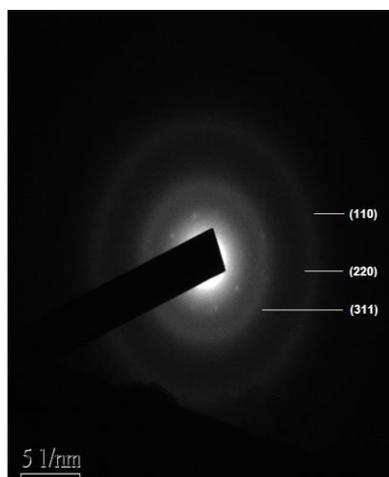


Fig 4

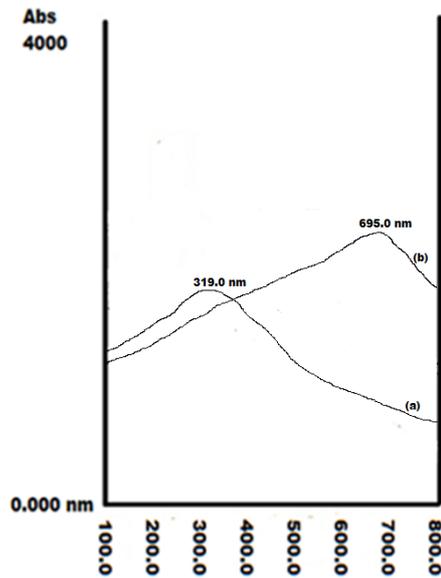


Fig 5

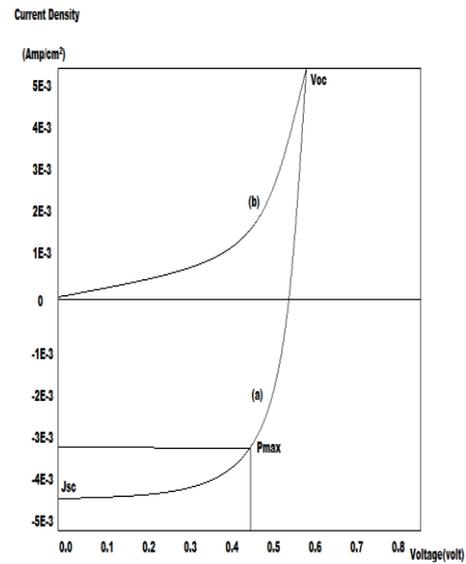


Fig 6

Current Density

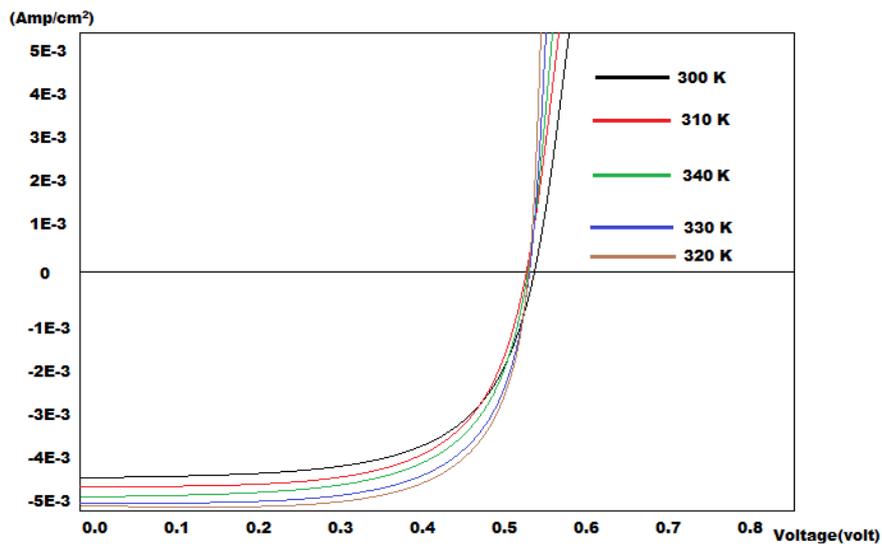


Fig 7

Fig 8