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OPTICAL PROPERTIES OF CdS/CuS & CuS/CdS HETEROJUNCTION THIN FILMS DEPOSITED BY CHEMICAL BATH DEPOSITION TECHNIQUE

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CdS/CuS and CuS/CdS thin films were deposited on glass substrates at room temperature by chemical bath deposition technique. The structural characterization was done using Philips PW 1800 X-ray diffractometer (XRD) while the absorption coefficient (α) together with the band gap were determined using the absorbance and transmission measurement from a Unico uv-2102 PC spectrophotometer, at normal incidence of light in the wavelength range of 200-1000nm. The results of the optical characterization of CdS/CuS heterojunction thin films were compared with optical properties of binary thin films of CdS and CuS. The results show a clear deviation in the optical properties of the stacks of CdS/CuS thin films from the individual binary films that make up the stacks. The plot of $(\alpha h\nu)^2$ against (hν) showed that the materials have direct band gap values 1.70, 2.00, 2.10 and 2.30 eV for CuS, CuS/CdS, CdS/CuS and CdS respectively.

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1. Introduction

A material is said to be a thin film when it is built up as a thin layer on a substrate by controlled condensation of the individual atomic, molecular or ionic species either directly by a physical process or through a chemical and/or electrochemical reaction. Otherwise, it is a thick film. There are various techniques of producing thin films for scientific application, which include: physical vapour deposition (PVD) technique, chemical vapour deposition (CVD), electrochemical deposition (ECD), hybrid technique, and chemical bath deposition (CBD) technique [1,2].

Thin films occupy a prominent place in basic research and solid state technology. The use of thin film semiconductors has attracted much interest in an expanding variety of applications in various electronic and optoelectronic devices due to their low production cost. Thin film can be made of multi-component, alloy/compound or multi-layers coatings on the substrates of different shapes and sizes [3,4]. A heterojunction thin film is formed by joining two layers of semiconductors with differing band-gap energies. When the layers have the same conductivity type an isotype heterojunction is formed, whereas in an anisotype heterojunction, the layer conductivity type differs.

Cadmium Sulphide (CdS) is one of the most promising II-VI compound materials because of its wide range of application in various optoelectronic, piezo-electronic and semi conducting devices [5,6]. Thin films of CdS are of considerable interest for their efficient use in the fabrication of solar cells [7]. Because of its optical properties, CdS is used in CdTe devices as an optical window [7, 8]. However, poor conductivity as low as $10^{-8}(\Omega m)^{-1}$ have been reported [9]. In order to overcome this problem, annealing and doping are used [9 - 11]. Thin films of copper chalcogenides $(S/Se)_2$ of multinary compositions containing indium (In) or indium and gallium $(In_{1-x}Ga_x)$ are being pursued vigorously as candidate materials for solar cell application due to their band gaps in the appropriate region for high efficiency of conversion [11].

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In this study we successfully deposited a heterojunction thin films comprising of CdS and CuS thin films and carried out analysis of the optical properties with a view to finding its applicability.

2. Experimental details

A chemical bath deposition technique was employed in preparing CdS/CuS thin films on glass substrates at room temperature. The substrates used were glass slides with dimension 75 x 25 x 1 mm^3. These were pre-cleaned in hydrochloric acid washed in a detergent solution, rinsed with distilled water and drip dried in air.

CdS/CuS thin films were deposited using chemical bath deposition of CdS and CuS films respectively. CdS and CuS films were prepared by hydrolysis of thiourea in an alkaline solution containing cadmium and copper salt solutions in the presence of OH^- ions respectively.

For the deposition of the CdS, bath A was prepared by mixing solutions of 2ml of 0.1M $CdCl_2$, 4ml of $NH_{3\,(aq)}$ solution, 4ml of 0.05M Thiourea and 2ml of 0.02M NaOH. The resulting solution was made up to 40ml with distilled water in a 50ml beaker. It was stirred vigorously for some seconds to obtain a homogenous solution. The substrates were then inserted and suspended vertically from synthetic foam, which rest on top of the beakers containing the solutions. After about 2½ hours, the substrate covered with an orange-yellow deposit, was taken out, rinsed with distilled water and drip dried in air.

For the deposition of the CuS, bath B was prepared from a solution mixture of 5ml of 1M $CuCl_2$, 2.5ml of 60% triethanolamine (TEA), 5ml of 1M Thiourea (TU) and 5ml of 30% NH_3. The resulting mixture was carefully stirred and made up to 45ml with distilled water in a 50ml beaker. The substrate was inserted using the above method, and allowed in the solution for 5 hours before removing; rinsed with distilled water and drip dried in air.

The formation of CuS/CdS and CdS/CuS heterojunction was achieved by dipping the substrate with its deposit from bath A in a fresh bath of B and vice versa. The formation of the heterojunction lasted for 2hours deposition time.

The structural properties of the thin films of CuS/CdS and CdS/CuS deposited in this work were studied by using Philips PW 1800 XRD. The absorption coefficient (α) together with the band gap was determined using the transmission and absorption measurement carried out with unico UV-2102 PC spectrophotometer.

3. Results and discussion

3.1 X–Ray Diffractormeter (XRD) analysis

Fig. 1 gives the XRD patterns of thin films of CdS/CuS and CdS/CuS deposited in this work. The thin films were scanned continuously between 0 to 75 at a step size of 0.03 and at a time per step of 0.15sec. Phase identification was then made from an analysis of intensity of peak versus 2θ. The films showed diffraction peaks at 2θ values of approximately 28^{o}C, 36^{o}C, 37^{o}C, 43^{o}C and 43^{o}C. The peaks at 28^{o}C correspond to the diffraction peaks produced by CdS thin films [12] and that of 37^{o}C and 43^{o}C agrees with the peaks of CuS films [13]. This identification confirms the formation of CdS/CuS and CuS/CdS core-shell

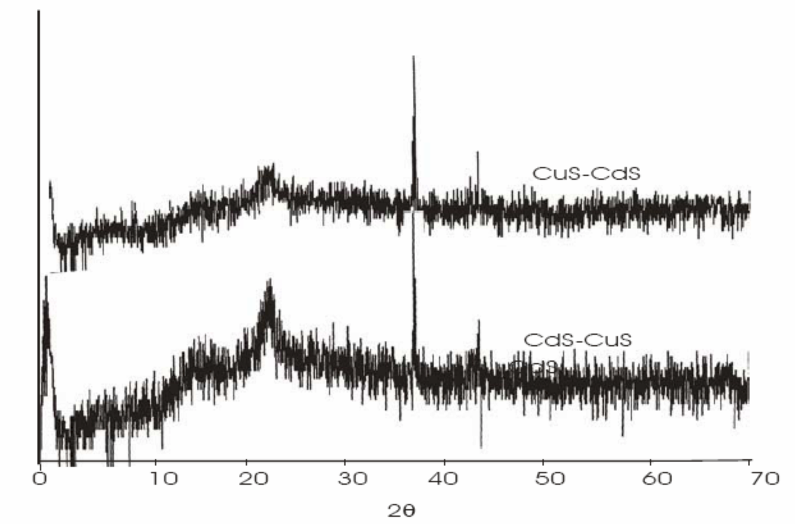

Fig. 1. XRD result for CdS-CuS thin films

3.2 Variation of absorbance and transmittance with wavelength

The optical absorption spectra of the films deposited onto glass substrate were studied in the range of wavelengths 200 – 1000nm. The variation of transmittance (%) and absorbance (A) with wavelength for the samples under study are shown in figures 2 and 3 respectively. The films show good absorption in the visible spectrum and a lower absorbance values in NIR region of the solar spectrum. The plot in figure 3 also reveals that CdS-CuS thin film has high absorbance values in the VIS and IR regions and virtually non-absorbing in the UV.

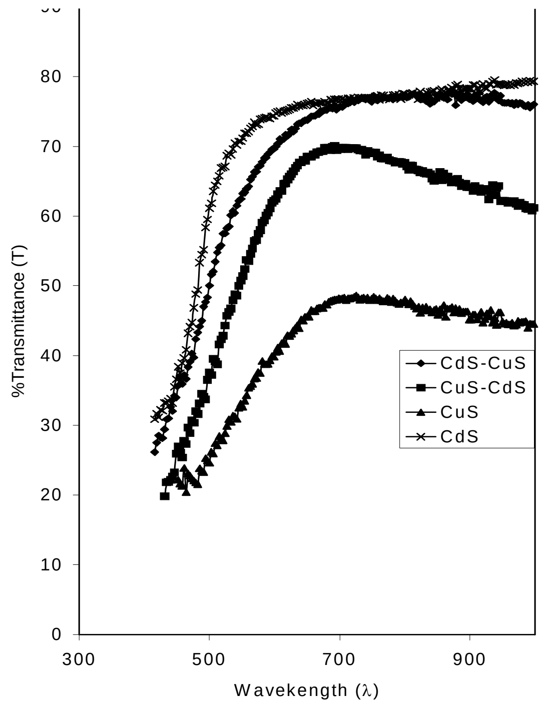

Fig. 2. Plots of transmittance (T) against wavelength (λ) to CdS-CuS thin films at various temperatures.

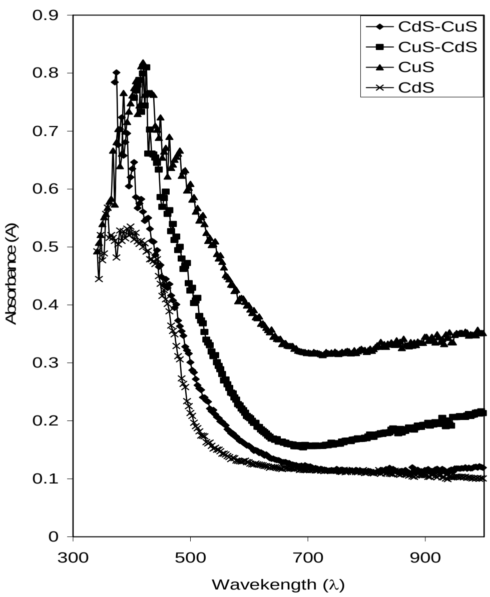

Fig.3: Pot of absorbance vs. wavelength (nm)

The transmission spectra displayed in figure 2 shows that the films transmit well in the NIR region of the solar spectrum. The film's transmittance increases gradually with wavelength in the VIS region of the solar spectrum and then decreases as the wavelength increases. Figures 2 and 3 show that the optical transmittance and absorbance of the core-shell; CdS-CuS and CuS-CdS thin films fall between the values obtained for CdS and CuS thin films with CuS thin film having the highest absorbance at any wavelength.

The details of the mathematical determination of the absorption coefficient (α) can be found in literature [14,15] while the plots of absorption coefficient against photon energy is shown in figure 4.

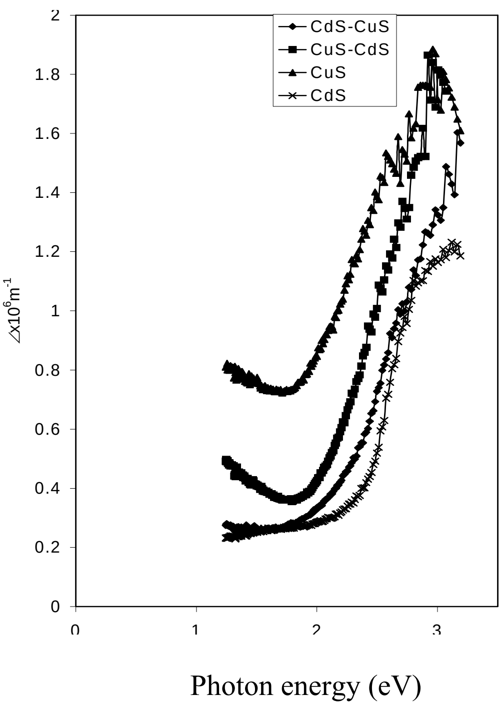

Fig. 4. Plot of absorption coefficient vs. photon energy.

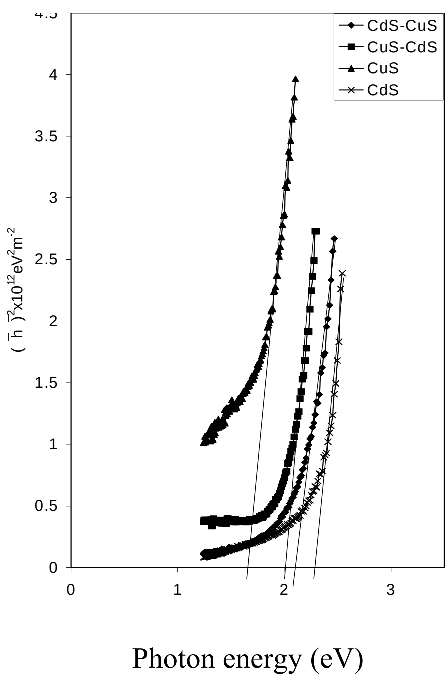

Fig. 5: Plot of $(\alpha h\nu)^2$ vs. hν.

The result revealed that there is generally low absorption at photon energy less than 2.0 eV. This shows that, the higher the absorbance, the higher the absorption coefficient and that there is more absorption rate at higher photon energy for the as grown films.

The absorption spectra, which are the most direct and perhaps the simplest method for probing the band structure of semiconductors, are employed in the determination of the energy gap, E_g. The E_g was calculated using the following relation:

$$\alpha = A(h\nu - E_g)^n / h\nu, \quad (1)$$

Where A is a constant, hν is the photon energy and α is the absorption coefficient, while n depends on the nature of the transition. For direct transitions n = ½ or ⅔, while for indirect ones n = 2 or 3, depending on whether they are allowed or forbidden, respectively.

The direct band gap of the films were obtained from the linear portion of $(\alpha h\nu)^2$ versus hν plot as shown in Figure 5. The direct band gap values are 1.70, 2.00, 2.10 and 2.30 eV for CuS, CuS/CdS, CdS/CuS and CdS respectively. CdS exhibits highest transmittance above 70% within the visible region and has a wider band gap of 2.30 eV, which agrees well with the values 2.38-2.45eV[16] and 2.37eV[17] reported elsewhere. The value obtained here for CuS also agrees well with the value reported in literature for crystals of Cu_xS[18]. A close observation of figure 5 shows that forming a heterojunction between CdS and CuS thin films enables the fabrication of materials whose band gap energy falls in between the values reported for the individual binary thin films making up the core shell. This is thus a way of achieving band gap tuning in semiconductor materials and hence the development of new materials for efficient photovoltaic application.

4. Conclusions

A heterojunction thin film comprising of CdS-CuS have been successfully deposited onto glass slide using chemical bath deposition technique. The XRD analysis reveals that the deposited films were composed of CdS and CuS. The optical studies showed that most of the films have high absorbance in the VIS region of the solar spectrum and high transmittance in the NIR region and therefore can be used as solar control device or selective absorber surface device. A comparison of the band gap energy of the deposited heterojunction thin film with the individual binary system shows that the obtained band gap energy falls in between the values obtained for the binary films.

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