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EFFECT OF GROWTH VOLTAGE ON ELECTRODEPOSITED CdS THIN FILMS USING UV VISIBLE SPECTROPHOTOMETER

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ABSTRACT
In Electrodeposition, six (6) parameters are necessarily considered during the deposition of the material layers. These are: pH, concentration of ions, time, deposition voltage, stirring and temperature. Four glass/FTO substrates were used to grow the CdS layers using 2-electrode electrodeposition (ED) method at different growth voltage, V_g (i.e 1400, 1300, 1200 & 1100) mV. The resulting films were then examined for optical characterization using UniCamp Spectrophotometer. The optical absorption measurement shows the value of bandgap, E_g for the film deposited at V_g 1300 mV has a bandgap of 2.43 eV which is close to the bulk material. The values of refractive index, extinction coefficient and absorption coefficient were generally lower at this particular V_g. The highest transmittance of >60% was observed for the layer grown at 1300 mV from optical transmittance spectra. The results suggest that the crystallinity of thin films decreases when the films are deposited at higher and lower voltages.
Key-words: CdS, Thin Films, Growth Voltage, Electrodeposition, two-electrode system

INTRODUCTION

The cheapest source of energy on earth and most environmentally friendly is solar energy which is primarily derived from the sun (Diso *et.al.*, 2010). Muhamed 2015, Reported that, the sun is one of the biggest stars which is about 1.39×10^8 km in diameter and its mass is about 98.6% of the mass of all the stars in the solar system. The average distance of the sun from the earth is approximately 1.5×10^8 km which is slightly higher than its diameter, and its light travels this average distance in 8 minutes 19 seconds (Wikipedia, 2021). The chemical elements primarily contained in the sun's mass are: hydrogen which is about 74% and helium 25%; the remaining 1% is made up of trace quantities of heavier elements (Kalogirous, 2009).

The solar energy reaching the periphery of the earth's atmosphere is considered to be constant for all practical purposes; this is called the **solar constant** and has a value of ~1.353 kWm^{-2} (Diso, 2011). The solar constant is estimated based on the solar radiation received on a unit area exposed perpendicularly to the rays of the sun at an average distance between the sun and the earth. All life on the earth is supported by the energy received from the sun through solar radiation via photosynthesis, the earth's climate and weather derived from it. The device that converts solar energy into electrical energy is the solar cell and it works by converting the solar energy received directly into electrical energy by a process termed as photovoltaic (PV) effect (Mohammad, *et.al,* 2015). It was reported that, the interaction of photons with material properties or certain material excitation generates voltage, which produces electric current (Sze and Kwok, 2007). Echendu and Dharmadasa (2013) reported that, the optical response of these devices depends principally on the optical properties of the constituent materials, which therefore determine how effectively and efficiently they can generate useful photons or convert photons into useful electron-hole pairs as the case may be.

Cadmium Sulphide (CdS) is among the binary compounds of the group II-VI family and its thin-film are widely used such as light-emitting diodes, optoelectronics device and solar cells (Izgorodi *et. al.,* 2010). It is an organic compound that occurs as a yellow solid naturally with two crystal structures as rare mineral green, necktie and hawlevite (Gadalla *et.al.*, 2022). Several methods have been used to deposits CdS thin films ranging from wet to dry methods (i.e Electrodeposition, chemical bath deposition, spray pryrolysis, molecular beam epitaxy, sputtering etc) (Dharmadasa *et. al.,* 2014).

CdS, being a window layer, is exposed to the incident radiation and absorbs light of a short wavelength which the rest is transmitted through to the absorber materials. A CdS layer provides a better nucleation surface for the absorber layer to grow uniformly and contributes to the internal electric field necessary for the separation of photo-generated charge carriers to prevent recombination within PV cells. In its PV application, CdS has been used as an n-type heterojunction partner to CdTe (Dharmadasa, 2018), Cu_xS and Cu $(InGe)Sl_2$ (CIGS) (Hamood, Abd El-sadek and Gadalla, 2018) solar cells.

In Electrodeposition, six parameters are necessarily considered during the deposition of the material layers. These are: pH, concentration of ions, time, deposition voltage, stirring and temperature. The method is suitable for fabricating macro-electronic devices such as PV solar cells and display panels (Diso et. al, 2013). It is also an ideal low-cost technique for growing nano-materials for the development of new nano-devices. One of the reasons for the use of a two-electrode system in this research is to eliminate any possible contamination of deposition electrolytes by ions such as Ag^+ and K^+ which may eventually leak into the bath from the commonly used Ag/ACl and Ag/HgCl (SCE) reference electrodes during the Electrodeposition process. Four glass/FTO substrates were used to grow the CdS layer at different growth voltages (1400, 1300, 1200 and 1100) mV. The deposition time, pH, stirring and concentration remain the same for all the samples. This paper presents a summary of experimental results obtained on electrodeposited CdS deposited at various growth voltages.

EXPERIMENTAL PROCEDURE

In this section the experimental procedures adopted in obtaining the data for the analysis was presented.

Electrodeposition of CdS Films

Thin films CdS were cathodically electrodeposited onto glass/FTO substrates at ~40^0C with an aqueous solution (pH = 2.00) containing 0.3M of $CdCl_2.7H_2O$ and 0.03M of $Na_2S_2O_3.5H_2O$. Fluorine doped tin oxide (FTO) coated conducting glass substrates with sheet resistance 7Ω/square were used as substrates. These were cleaned in organic solvent (acetone and methanol) and finally rinsed in de-ionized water. Details of the experimental procedure for the growth of CdS have been discussed elsewhere (Diso *et. al.,* 2010).

Measurement Techniques

A PerkinElmer UVWinLab 6.0.4.0738 spectrometer is used for investigating the optical properties and their constant. The optical parameters were determined from normal-incidence transmission spectra of the layers using the equation below. The bandgap energy and transition type can be derived from the Stern relationship (Sze and Kwok, 2007).

$$\alpha = \frac{c(h\upsilon - E_g)^{\frac{1}{2}}}{h\upsilon} \qquad (1)$$

Where *c* is a constant, *h* is a plank's constant, and *v* is the frequency of the incident light.

The absorbance and absorption coefficient are also related to the transmittance (Kittle, 1996).

$$A = \log_{10}\left(\frac{1}{T}\right) \qquad (2)$$

or

$$\alpha = -\frac{\ln T}{d} \qquad (3)$$

Where *d* is the thickness of the thin film, *A* is the absorbance and *T* is the transmittance.

The refractive index; *n* plays an important role in the search for optical materials. It is also used to determine the propagation of velocity of photons in the materials. The value of *n* was calculated using the relation (Kittle, 1996).

$$R = \frac{(n-1)^2}{(n+1)^2} \qquad (4)$$

Where *R* is the normal reflectance

A measure of the rate of the reduction of transmitted light through a substance can be obtained using the extinction coefficient, *k* as (Kittle, 1996).

$$k = \frac{\alpha\lambda}{4\pi} \quad (5)$$

Where λ is the wavelength

RESULTS AND DISCUSSION

The results obtained are discussed in this section.

Visual Appearance

Plate 1 shows the visual appearance of CdS layers deposited as a function of growth voltage. As shown in the plate, at higher cathodic voltage, the sample become dark which are attributed to the Cd richness. Similarly, at lower cathodic voltage, the layer appears light yellow, indicating S richness. In the intermediate voltages the layers appear orange-yellow, similar to the bulk CdS material. The formation of CdS on the cathode can be represented by the following mechanisms.

$$Cd^{2+} + S_2O^{2-} + 2\overline{e} \Leftrightarrow CdS + SO_3^{2-} \quad (6)$$

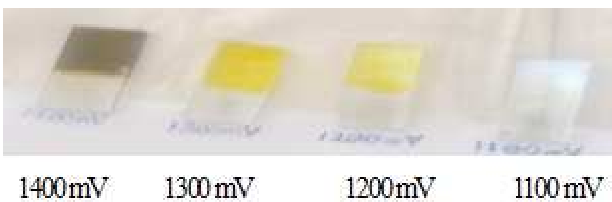

Plate 1: As deposited ED-CdS thin films on glass/FTO substrates of different growth voltage

Optical characterization

Optical Absorption

Optical Absorption studies were carried out to extract the optical energy bandgap (E_g) of these layers. The values of E_g were determined using equation (1) (see Fig. 1). The values obtained for the material layer are shown in Table 1. The changes in absorption edge as a function of growth voltage are noteworthy. The light yellow of material layer growth at a low cathodic voltage (1100mV) shows a poor absorption edge. The dark-orange layers (V_g = 1300 and 1200) mV show a steep and improved absorption property. The reason for the absorption edge sharpening might be due to a change in the stoichiometry or reduction of intrinsic defect population and improved crystallinity, which darker materials again deteriorate the optical absorption. Similar observation was reported from literature by (Diso et. al., 2010; Echendu et. al., 2014, Ojo et.al 2018).

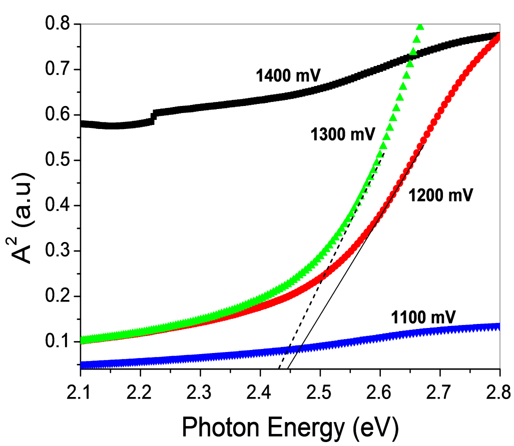

Figure 1: Optical absorption curves for CdS deposited at different growth voltages.

Table 1: Bandgap energies as a function of growth voltage of CdS film.

S/N	Growth Voltage (mV)	Bandgap energy (eV)
1	1400	0
2	1300	2.44
3	1200	2.45
4	1100	0

Transmittance

The normal-incidence transmittance spectra of electrodeposited CdS layers deposited of various growth voltages are shown in Figure 2. Measurements were taken in the wavelength range of 200-800nm the deposited films. The transmission coefficient for deposited CdS layers grown at 1300mV exhibited transmittance of ~40% in the visible region, at an absorption of 512nm. It also noted that; transmittance increases as incident photon wavelength increases. Furthermore, all the samples deposited at various V_g have pinholes except for ED-CdS at V_g ~1300mV. Metin and Esen (2003) reported that, a shaper absorption edge indicates fewer defect and impurity energy levels in the film.

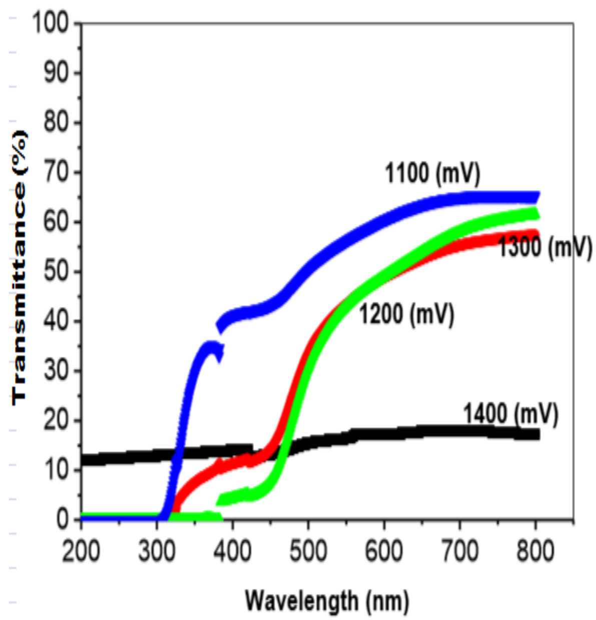

Figure 2: Graph of the transmittance versus wavelength at different growth voltages

Refractive Index (*n*)

Figure 3 presents the refractive index of the CdS layers as a function of the energy bandgap. As seen from the figure, the refractive index decreases for all the samples as the energy bandgap increase. Furthermore, at a higher energy bandgap, in the ultraviolet region, the refractive indices of all the samples tend to become very close to one another. The refractive index of the sample deposited at V_g 1300mV is ~0.20 which is the least value compared with the remaining samples except for the one deposited at V_g 1400mV which is the most insignificant. Thus, a decrease in the *n* value means an increase in the velocity, *v* at which light propagates in the layer (Kitte, 1996). Therefore, the light will propagate faster in the CdS samples deposited at V_g ~1300mV.

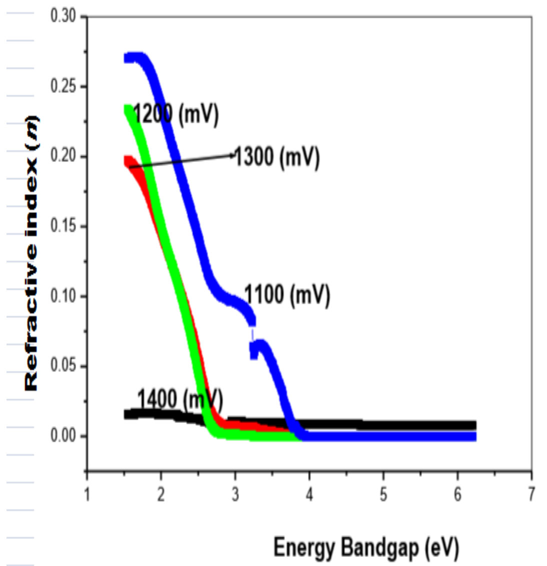

Figure 3: Graph of the refractive index versus wavelength of different growth voltages.

Absorbance

The absorbance response of the ED-CdS samples deposited at various V_g is shown in Figure 4. The absorbance generally increases as the wavelength of the incident radiation decrease. The samples deposited of V_g at 1200mV and 1300mV have similar absorbance patterns showing absorption edge at the same photon wavelength of 512nm. Similarly large scatter in the absorbance was observed for the samples deposited at V_g 1400mV and 1100mV. The samples even show significant absorption in the long-wavelength region. A similar observation was reported by Echendu *et.al.,* (2017) and Aliyu *et.al.,* (2013)

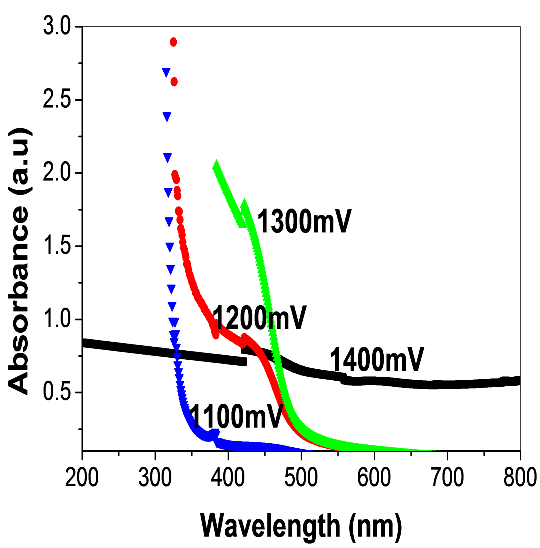

Figure 4: Optical absorbance curves for CdS deposited at different growth voltages.

Extinction Coefficient (*k*)

Figure 5 shows the extinction coefficient versus energy bandgap for the ED-CdS layers. Sample deposited at V_g 1400mV shows different results with respect to the remaining ones, this may be due to the quality of the layer (black) in which light absorbs more (Sze and Kwok, 2007). The values of k for the samples deposited at V_g 1200mV and 1300mV coincide at the same energy bandgap of ~2.45eV. From the figure, the CdS layer deposited at these V_g become more stable and improved in quality. Echendu *et.al.,* (2017) reported a similar observations

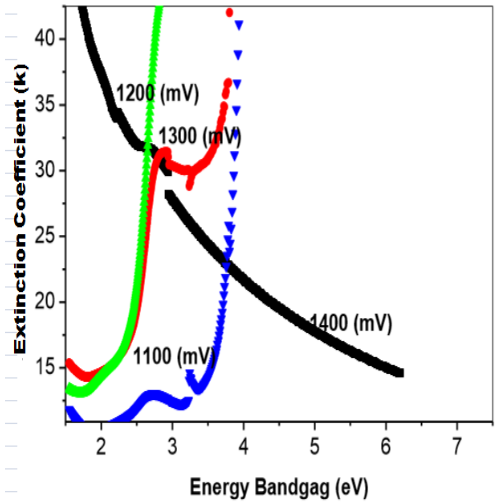

Figure 5: Graph of the extinction coefficient versus energy bandgap at different growth voltages.

CONCLUSION

Electrodeposition of CdS thin films using a simple two-electrode system was demonstrated. The optical properties of the deposited films were found to vary at various deposition voltages in the wavelength range of 200nm to 800nm, showing high quality ED-CdS films obtained at 1300mV. The results obtained show that growth voltage is one of the key parameters to consider during deposition of the material layers.

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