Annealing and Surface Treatment Effect on the Optical and Electrical Properties of n-Type CdS Binary Compound Semiconductors

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Abstract - The preparation of CdS thin films were actualised with electrodeposition technique using cathodic voltage of 1200 milli – Volts (mV). The optical and electrical properties of three different classes of CdS semiconductors namely as – deposited CdS layers (AD-CdS), CdS layers heat-treated in air without any chemical treatment (HT-CdS) and CdS layers treated with CdCl2 and annealed in air (CC-CdS) have been investigated in this work. Results from optical analysis showed that AD-CdS layers have the least absorption edge and highest energy bandgap. Annealing the CdS thin films without and with CdCl2 treatment brings the energy bandgap to same value of ~2.42 eV. The main distinction between the HT- and CC-CdS layers is that the absorption edge of CC-CdS films is sharper than the HT-CdS. Results from electrical analysis revealed that the magnitude of photo-electro-chemical (PEC) cell signals which give a clue about the doping concentration of the semiconductor material is greater in CC-CdS layers than in AD- and HT-CdS layers. It has been experimentally proven by researchers that electronic devices like solar cell devices developed using AD-CdS thin films produce very poor results while the cells developed using HT-, and CC-CdS layers yield better efficiency (Abdul-Manaf, 2015). It is therefore vital to study some of the properties of these materials which make them behave differently. For this reason, UV-Visible spectroscopy and photo-electro-chemical (PEC) cell measurement techniques have been selected to investigate the optical and electrical properties of the AD-, HT- and CC-CdS thin film semiconductor materials respectively.

1 INTRODUCTION

CdS is a renowned compound semiconductor which belongs to the II-VI family and it has wide applications in opto-electronic devices. The electrical conductivity type of un-doped CdS is n-type and this has been attributed to intrinsic donor defects like cadmium interstitials and sulphur vacancy (Salim et al., 2016; Wu et al., 2010). The bandgap energy of bulk CdS layers measured at room temperature is 2.42 eV (Chu, 1992; Wu et al., 2010). Due to its higher energy bandgap, it has been established to serve as appropriate window layers to certain semiconductor materials with lesser bandgap when used in solar cell applications. Some of these low-bandgap materials are Copper Indium Gallium Selenide (Chaur et al., 2005) and CdTe (Dharmadasa et al., 2002; Olusola et al., 2017).

Due to the fact that electrons are the majority carriers in n-type CdS semiconductors, it is therefore of utmost importance for these majority charge carriers to contribute to the current flow in the material. One essential way of realising this is to thermally promote electrons in the valence band into the conduction band. Annealing the semiconductor material in air without and with chemical treatment is one of the probable means of achieving the electron thermal excitation. Since surface treatments and annealing are vital processing steps which determine the appropriateness of thin film materials for electronic device applications, it is therefore expedient for the semiconductor materials to go through these processing steps so as to improve their electrical conductivity and achieve optimum performance.

In this work, three different classes of CdS layers have been explored and intrinsic approach has been used to improve the electrical conductivity of CdS thin films. The three classes of semiconductor materials considered are: as-deposited CdS (AD-CdS), heat-treated CdS in air with no chemical treatment (HT-CdS) and CdCl2 heat-treated CdS in air (CC-CdS).

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of using annealing temperature and duration of 400°C and 20 minutes respectively originated from researchers in the field of semiconductor technology who have experimentally shown that annealing conditions of 400°C for 20 minutes is suitable for post growth treatment of CdS thin films. Abdul-Manaf et al., (2015) and Salim et al., (2016) annealed their CdS layers using annealing conditions of 400°C for 20 minutes. Ojo and Dharmadasa (2016) were able to achieve the highest conductivity values of CdS layers at heat-treatment conditions of 400°C for 20 minutes. Furthermore, from the Schottky contacts made by Ojo and Dharmadasa (2016), the authors were able to obtain the highest potential barrier height and least ideality factor under these annealing conditions.

3 RESULTS AND DISCUSSION ON OPTOELECTRONIC FEATURES OF ELECTRODEPOSITED CdS THIN FILMS

Two fundamental techniques namely UV-Visible spectroscopy and photo-electro-chemical (PEC) cell measurement techniques have been used in this work to examine the optical and electrical properties of electroplated n-CdS semiconductors respectively. Some of the other characterisation techniques carried out on CdS layers are scanning electron microscopy for investigating the surface morphology of the thin film, X-ray diffraction technique for investigating the material structural property and these have been reported in (Olusola, 2016).

3.1 OPTICAL ABSORPTION STUDY

The bandgap energy of AD-, HT-, and CC-CdS thin films were determined from the results of optical absorption study. Figure 1 shows the optical absorption curves of AD-, HT-, and CC-CdS thin films deposited at growth voltage ($V_g$) of 1200 mV. The extrapolation of best tangent of the absorption curves to the photon energy axis when $A^2=0$ gives the bandgap of the desired materials.

![Graph showing optical absorption curves for AD-, HT-, and CC-CdS layers](image_url)

Fig. 1: Optical absorption curves of AD-, HT- and CC- CdS layers deposited at cathodic voltage of 1200 mV

In Figure 1, the bandgap of AD-CdS grown at $V_g$=1200 mV is ~2.50 eV; after heat-treatment in air without and with CdCl$_2$ treatment, the bandgap decreased to ~2.42 eV. As illustrated in Figure 1, AD-CdS films have larger bandgaps than the HT-, and CC-CdS films. Particles at nano—size levels can be a possible reason for the larger bandgap values seen in AD-CdS thin films. The presence of quantum confinement effects in the opto-electronic properties of semiconductor nanoparticles enables them to possess larger bandgap. (Ravindran et al., 1999). The bandgap of nanoparticles are large (Ravindran et al., 1999; Wu, 2004) with enormous surface to volume ratio (Fonash, 2010). Nanda et al., (1999) reported that smaller crystallite sizes are features of semiconductors with huge surface to volume ratio. However, quantum effects are observed only for crystallites ≤ 10 nm. If the surfaces of the substrates on which the films are deposited are not fully covered by the deposited layers, it can also lead to larger bandgap occurrence. This is because existence of gaps in-between crystallites can permit wavelengths ranging from ultraviolet, to visible and infrared region of the solar spectrum to pass through thus producing larger bandgap values.

Apart from the energy bandgap of semiconductor, the absorption edge is also an important optical characteristic which is worth looking at. The description given by Han et al. (2011) illustrates the importance of semiconductors with sharp absorption edge. The authors noted that semiconductors will have low amount of defects and impurities in the energy levels if the absorption edge is sharp. By visually observing the absorption spectra in Figure 1, it can be seen that the absorption edge of CC-CdS is sharper than those of the HT, and AD-CdS layers. The lower absorption edge in AD-CdS thin films can be caused by the existence of enormous defects in the as-grown semiconductor materials and this makes them inappropriate for use as a window material in CdS/CdTe based solar cells (Abdul-Manaf, 2015; Han et al., 2011). The enhancement in the absorption edge of CC-CdS thin films is a sign that the CC-CdS thin films are more crystalline and suitable semiconductor materials than the AD-CdS layers for solar cells application (Olusola et al., 2016).

3.2 ELECTRICAL STUDY

Study on how the AD-, HT-, and CC-CdS semiconductor materials behave electrically was carried out by using photo-electro-chemical cell measurements. While taking the PEC cell measurements, both the sign and magnitude of the values obtained are of great interest. The electrical conduction type of the semiconductor is gotten from the PEC signal sign. For instance, when the PEC signal is positive, it shows a p-type semiconducting layer. Likewise, when the PEC signal is negative, it shows an n-type semiconducting layer. Qualitative information about the doping density of the semiconducting materials can be obtained from the PEC signal magnitude (Dharmadasa, 2013). Intrinsic semiconductors, insulators and metals show approximately zero PEC signals. The zero PEC signals in metals arise as a result of their very narrow depletion width while the zero PEC signals observed in intrinsic semiconducting materials and
Insulators are due to their large depletion region (Salim, 2016). When a semiconductor has optimum doping concentrations, large PEC signals are observed; a highly-doped semiconductor is known to have very poor PEC signals (Dharmadasa, 2013).

PEC cell measurement technique was used to determine the type of electrical conductivity possessed by CdS layers electroplated within the cathodic potential range of 1150 – 1250 mV. The PEC signals of the AD-CdS, HT-CdS and CC-CdS layers possess electrical conductivity of n-type as illustrated in Figure 2. The results in Figure 2 thus showed that despite the variations in the magnitude of PEC signals of the explored CdS layers; all CdS thin films are n-type regardless of the treatment condition and growth voltage. The n-type nature of CdS thin films which are not doped with external elements have been attributed to the existence of intrinsic defects such as sulphur vacancies and cadmium interstitials in the CdS crystal lattice structure. (Wu et al., 2010; Yilmaz et al., 2015).

The main difference among the AD-, HT- and CC-CdS layers can be seen in the magnitude of the PEC signals as revealed in Figure 2. With respect to the magnitude, the maximum PEC signals were observed in the CC-CdS layers followed by the HT-CdS layers. The least PEC signals were seen in the AD-CdS layers. The PEC cell signals in Figure 2 thus remain n-type while the magnitude changes as the condition in which the material is subjected to varies from as-deposited state to state of heat-treatment without and with CdCl₂.

![Figure 2: Typical PEC signals of as-deposited (AD), heat-treated (HT) and CdCl₂ heat-treated (CC) CdS layers deposited at cathodic voltages ranging between 1150 and 1250 mV.](http://dx.doi.org/10.46792/fuoyejet.v4i3.523)

The PEC cell results illustrated in Figure 2 plainly specifies the tendency of moving from low n-type towards high n-type. The drifting from low n to high n is an indication of changes in the doping concentration of the semiconductor material. Thus Figure 2 clearly shows that the doping concentration changes from low n-type towards high n-doping. These variations can be mostly explained in terms of re-arrangements of defects in the semiconductor materials. Cha et al., (2004) further explained that annealing of CdS thin films lead to elimination of impurities and formation of sulphur vacancy. It should be recalled that sulphur vacancy is one of the intrinsic donor defects in CdS films; therefore, annealing enables the material to become more n-type if sulphur vacancies are generated via this process.

### 4 CONCLUSIONS

Conclusions resulting from this work are emphasised below:

1. Results from optical analysis showed that the energy bandgaps of AD-CdS, HT-CdS and CC-CdS thin films are ~2.50, 2.42 and 2.42 eV respectively. These results thus revealed that as-deposited CdS semiconductors have higher energy bandgap than CdS layers annealed without and with CdCl₂ treatment.

2. The least absorption edge slope was seen in AD-CdS layers while CC-CdS layers have the highest absorption edge slope. The absorption edge slope for HT-CdS lie in-between that of AD-CdS and CC-CdS. This study showed that CC-CdS layers are better materials for fabrication of electronic devices than the AD-, and HT-CdS layers because of their sharper absorption edge.

3. Results from photo-electro-chemical cell study revealed that the three classes of CdS semiconductors (AD-CdS, HT-CdS and CC-CdS) explored in this work were all n-type in electrical conduction. Annealing without and with CdCl₂ treatment improve the size of the PEC signals but does not change the conductivity type.

4. The magnitude of PEC signals which is an indication of the material doping density is higher in CC-CdS layers than in AD- and HT-CdS layers. This experimental investigation thus signifies that the density of electron which contributes to conduction current is higher in CC-CdS layers than AD- and HT-CdS layers.

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