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Photosensitivity and Physical Properties of ITO/CdSe/Ag Thin Films Growth by CBD Technique

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Abstract: Cadmium Selenide (CdSe) thin films of different thickness were deposited on ITO (Indium-Tin Oxide) and glass substrates using the Chemical Bath Deposition (CBD) method at 50^oC and 3h time, which employs a bath containing Cadmium acetate ($(CH_3COO)_2Cd.\ 2H_2O$) and Sodium Selenosulfate (Na_2SeSO_3) solution as a source of Cd^{+2} ions and Se^{-2} ions respectively. The cleaned substrates were immersed at an oblique angle~(15^o -20^o) in the final solution. The optical and electrical characteristics of these thin films were investigated using a UV-Vis spectrophotometer and a silver probe setup with a current-voltage (I-V) source meter. Optical studies revealed that the CdSe thin films had a straight band gap that decreases with thickness from 2.14 to 1.9 eV.The electrical study (I-V characteristics) revealed a linear relationship between voltage and current, indicating the formation of ohmic contact between the conduction electrodes (Ag and ITO) and the semiconducting CdSe layer. Furthermore, increasing the illumination intensity from (30-60 watts) increases the sensitivity of the film to light, resulting in the formation of electron-hole pairs that contribute to conduction. Furthermore, when the thickness of the CdSe film increases, the photosensitivity increases from (0.21-0.27) and (0.24-0.28) for 423nm and 631nm CdSe thin film thickness, respectively.

Keywords: Chemical Bath deposition, Electrical properties, ITO/CdSe junction, Optical properties, photosensitivity.

1. Introduction

Semiconductors are extremely important due to its wide application in electrical, optical, and other devices. Among the most significant semiconductors are the compounds of the periodic table group (II-VI), including the compounds that contain cadmium (Cd), such as (CdSe, CdS, CdTe) and others, which are characterized by having a wide and direct energy gap [1].Cadmium selenide (CdSe) is one of the most important semiconductor compounds that fall in to the Group II-VI of the periodic table, and it is widely used in optoelectronics due to its direct bandgap energy (1.74 eV) and optical absorption coefficient in the visible region of the solar spectrum. It is of the negative type (n-type), and it can be converted to the positive type (p-type) through doping[2] and [3].The CdSe film can be used in many applications, including solar cells [4], photodetectors[5], photosensors or photovoltaic solar cells [6], and thin-film diodes [7] or for a pn-junction [8], and it can be prepared using a variety of deposition methods, such as thermal evaporation [9], Successive Ion Layer Adsorption and Reaction Method (SILAR)[10], spray pyrolysis technique [11], Solvo thermal technique [12], Sol-gel technique [13], chemical bath deposition method [14].This is the method employed in this study to prepare the films. It is a simple and low-cost technique for creating films, and it is characterized by the preparation of thin films with large areas and nano forms, and the deposition temperature is low. Its deposition is based on ion-by-ion growth on the substrate not atoms, allowing it to coat a large number of substrates in a single experiment [15].

This study aims to prepare a photosensor by depositing a CdSe film on ITO substrates and using silver paste as a conductive electrode, therefore investigating the electrical characteristics of the film and determining the degree of the film's light sensitivity.

2. Materials and Methods:

2.1. Substrate Preparation

Because impurities have a considerable influence on the accuracy of the subsequent measurements, substrate cleaning is an important initial step.

2.1.1. Glass substrate preparation

Chinese-origin laboratory glass substrates with dimensions (0.1×1.2×7.5)cm were used to deposit the CdSe film on it due to its availability, low cost and high transparency. The substrates are first washed with laundry soap and left under flowing water for a few minutes to remove the laundry soap well, then placed in distilled water for 5 min, the substrates are immersed in hot ethanol at a temperature (70-80)^oC for 15 min to ensure that any organic matter is removed, then washed with distilled water and left in it for a few minutes, and finally immersed in acetone for several minutes and then left to dry, and it is weighted with a sensitive scale to be ready for use.

2.1.2. ITO substrate preparation

ITO (n-type) transparent conductive oxide coated glass substrates of dimensions (1.1 ×50 ×25) mm, with sheet resistance 15 Ohm/sq , and is Transmittance ~>80 %,were used for the purpose of depositing the CdSe thin film on them. They are first softly cleaned with laundry soap and flowing water, and then the substrates are kept under flowing water for a few minutes to remove the laundry soap completely. The substrates are then cleaned using an ultrasonic cleaning device (Sonication bath), where they are immersed in distilled water for 10 minutes in the device bath, followed by 20 minutes in an ethanol solution inside the device bath.Finally, it is immersed in acetone for a few minutes and let to dry before being weighed on a sensitive scale and stored in a vacuumed container to protect it from the atmosphere and the other factors affecting it.

2.2. Preparation solution of CdSe

To produce a CdSe film, Na_2SeSO_3 was prepared as a source of selenium ions Se^{-2} by mixing selenium powder Se =0.87gm in 10 ml distilled water with powdered sodium sulfite Na_2SO_3 = 2.6 gm in a reflux system with a magnetic stirrer and heated using a stirrer hot plate for (1.5-2) h at a temperature (70-75°C) and then filtered to remove insoluble substances and achieve a clear solution. Then, a solution of cadmium acetate is prepared as a source of cadmium ions Cd^{+2}, which is a white powder, by dissolving 2.04 gm of it in 10 ml of distilled water, stirring with magnetic stirrer for 3 minutes, where a transparent solution accumulates and adding ammonia NH3 with a volume of (1.5-2) ml Depending on the intensity of the ammonia concentration, the color of the solution changes and becomes white translucent, and 3 drops of TEA are added with constant stirring.Finally, a solution of Na_2SeSO_3 is added to the second solution, and the color of the solution becomes orange. The solution's volume is then completed to 100 mL by adding distilled water. The resulting solution is then homogenized by mixing it for 5 minutes using a magnetic stirrer. After that, the cleaned substrates are immersed in the final solution at an oblique angle ~ (15-20)° for 3 hours at a temperature of 50°C by using CBD method.This method is based on the slow release of Se^{-2} and Cd^{+2} ions after immersing the substrates in the final solution. The below equations describe the mechanism of forming a CdSe film[16].

$Na_2SeSO_3 + OH^{¨} \longleftrightarrow Na_2SO_4 + HSe^-$

$HSe + OH^{¨} \longleftrightarrow H_2O + Se^{-2}$

$(CH_3COO)_2Cd.\ 2H_2O + 4NH_3 \longleftrightarrow [Cd\ (NH_3)_4]^{+2} + (CH_3COO)_2^{-2} + 2H_2O$

$[Cd\ (NH_3)_4]^+ \longleftrightarrow Cd^{+2} + 4NH_3$

$Cd^{+2} + Se^{-2} \longleftrightarrow CdSe \downarrow$

One of the factors influencing the film's characteristics is its thickness. Thickness of the prepared films was determined using the weights method. This is achieved by employing a sensitive scale to weigh the substrates before and after deposition and using the following relationship [17]:

$t = m/\rho A$ .... (1)

Wheret represents the thickness, ρ represents the density of the CdSe film and equal (5.816 gm/cm^3), m represents the film mass, and A represents the film area.

3. Results and discussion:

3.1. Optical characteristics

The optical properties of CdSe films prepared on glass and ITO substrates were studied using a spectrophotometer (721-2000 UV-Vis-NIR), where the optical absorption spectrum of the prepared films was studied within the wavelength range (340-1000nm), the energy gap (Eg) is computed by projecting straight line from exponential part of the curve $(\alpha h\nu)^{1/r}$to the hν axis with r = 1/2. The plot of $(\alpha h\nu)^2$ vs. hν for CdSe films as shown in Fig. (1).which shows the relationship between the square of the absorption coefficient and the energy of a photon, based on the Tauc's relationship [18]:

$\alpha h\nu = A\ (h\nu - E_g)^r$…………………………….. (2)

Where A is a constant, Eg is the material's optical band gap, and the exponent r depends on the kind of transition. The r can have values of 1/2, 2, 3/2, and 3 corresponding to allow direct, allowed indirect, forbidden direct, and forbidden indirect transitions, respectively. The CdSe film has a direct transmission r=1/2. The figure (1) shows that the Eg value of model (A) and the deposited on the glass substratesis (2.14 eV), the E_g of model (B) deposited on ITO substrateis (2.1 eV), and the E_g of model (C), which is also deposited on ITOis (1.9 eV), with different thicknessas shown in table (1) and nearly agree with [2] and [19],this thickness variation is due to the different stacking and growth of grains on top of each other during the thin film formation process [20].All these band gaps are higher than the value of Eg in bulk CdSe (1.7 eV) due to the quantum confinement effect [18].

Table(1): optical properties of CdSe thin film

samples	**Thickness(nm)**	**Energy gap(eV)**
A (glass)	368	2.14
B (ITO)	423	2.1
C (ITO)	631	1.9

The results in table (1) reveal that increasing the thickness of the film has an effect on the energy of the gap; as thickness grows, the energy of the gap decreases, which is agree with[21]. There are various explanations for this form of behavior. To begin with, the band gap value may be impacted by a variety of elements such as grain size, carrier concentrations, the presence of impurities, structural parameters, thin film lattice strain, and so on. There is a possibility that structural imperfections exist inside the thin films, causing an increase in the allowed states near to the conduction band within the forbidden zone. However, in the case of thick films, these states may mix with the conduction band, resulting in a reduction in band gap [21].

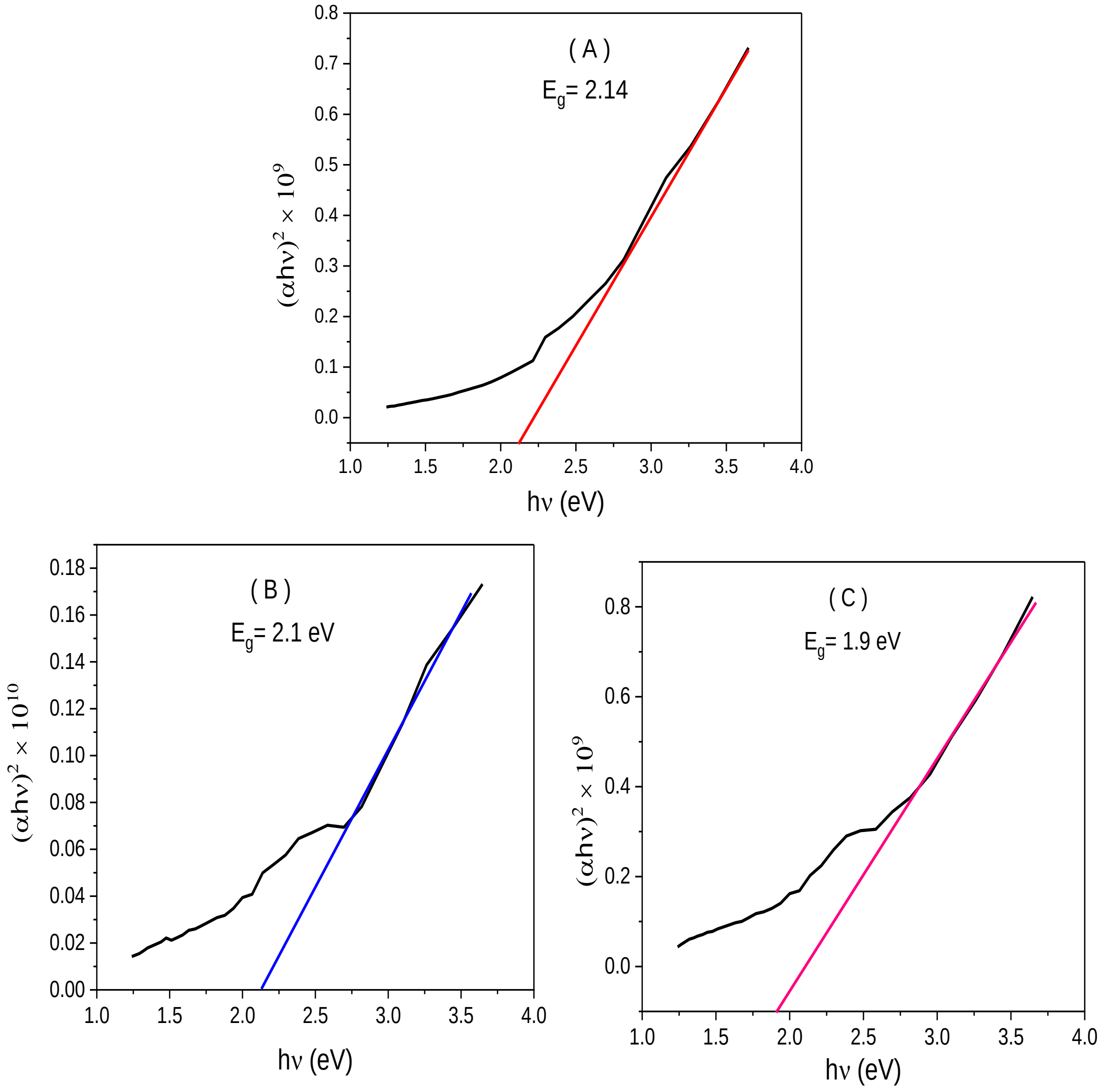

Figure (1): The energy gap of CdSe: (A) on glass substrate, (B) on ITO substrate at thickness 423 nm and (C) on ITO substrates at thickness 631 nm

3.2. Electrical and photosensitivitystudies:

The dark and light I–V characteristics curve of deposited CdSe films with different film thickness values and under different illumination intensities are shown in Fig.(2). Where CdSe was deposited on glass and ITO substrates, where ITO substrates are considered as a transparent conductive electrode and silver paste was chosen as another conductive electrode to ensure the good electrical conductivity of the films.The relationship in Fig.(2) demonstrates a straight linear behavior, which indicates the emergence of ohmic contact resulting from the conduction electrodes (Ag and ITO) with the semiconducting CdSe film (ITO/CdSe/Ag), and this is because ITO has a work function near to the conduction band edge of the CdSe films and the work function of silver metal is higher than that of the CdSe film, which aligns with the film valence band To avoid undesirable barrier generation[22].Also, when the intensity of illumination increases, the resistance falls, indicating that the incident photon's energy destroys some covalent bonds in the CdSe film, resulting in free electron-hole pairs that contribute to the generation of a current.

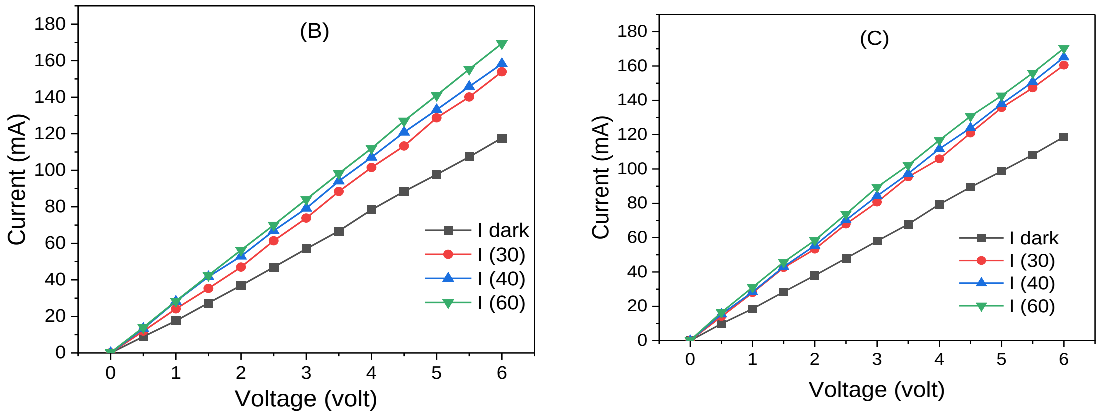

Figure (2): CdSe thin film I-V characteristics curve with varying illumination intensity at different thickness: Sample (B) and Sample (C)

The film's photosensitivity may be computed using the equation (3)[22][2]:

$$S = \frac{R_d - R_L}{R_d} \quad \cdots\cdots\cdots\cdots\cdots\cdots\cdots\cdots \quad (3)$$

Where R_L represents the resistance under illumination and R_d represents the resistance in the dark. Photosensitivity is an essential parameter that indicates how light sensitive the film is as well as the photosensor's quality. Figure (3) depicts the relationship between photosensitivity and light intensity. Where the photosensitivity steadily rises, photosensitivity of the films increases with light exposure, which may be attributed to the creation of electron-hole pairs that contribute to conduction. As a result of the findings, this film can be used as a sensor in solar cells and other photovoltaic applications.

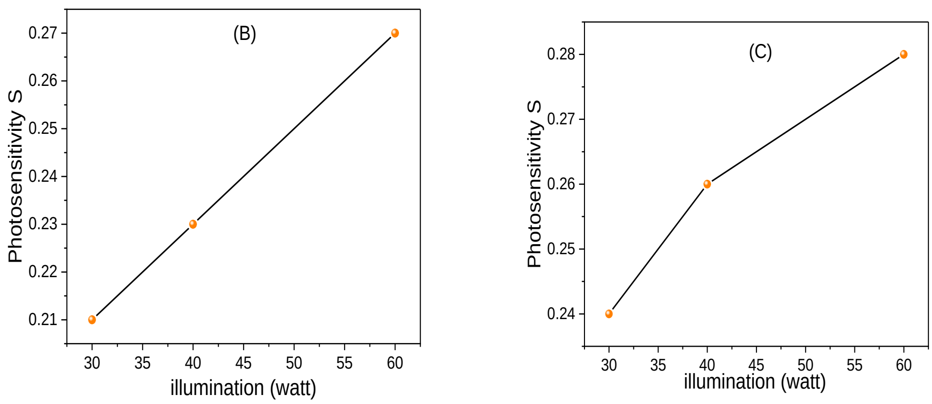

Figure (3): Photosensitivity with the illumination intensity of different thickness of CdSe thin film

3.3. Photosensitivity and Thickness:

Figure (4) depicts the relationship between photosensitivity and light intensity in deposited films of different thickness, where photosensitivity rises with thickness. The effective area of the sample grows as the thickness increases, resulting in a drop in resistance and an increase in conductivity. Furthermore, raising the thickness increases the light absorption region, increasing the formation of electron-hole pairs, which is agree with [23].

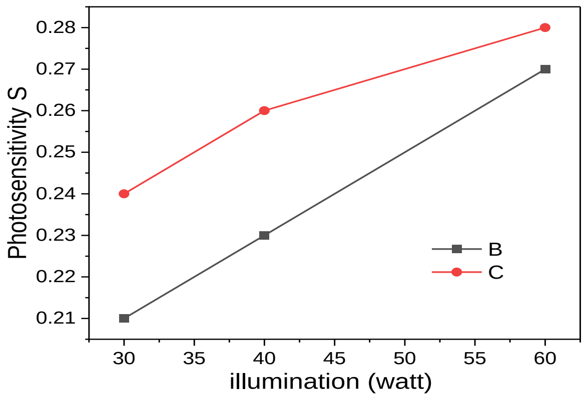

Figure (4): Comparison of photosensitivity for various thicknesses of CdSe thin film

Finally the illumination intensity with Photosensitivity for different thicknesswere listed in table (2).

Table (2): Illumination intensity with Photosensitivity of different thin film thickness

Illumination (watt)	**Sample (B)** **Thickness = 423 nm** **E_g = 2.1 eV**	**Sample (C)** **Thickness = 631 nm** **E_g = 1.9 eV**
30	0.21	0.24
40	0.23	0.26
60	0.27	0.28

4. Conclusion:

ITO/CdSe junction was successfully deposited by the CBD process at different film thicknesses. According to the optical investigation, the band gap value of thin film drops from (2.14-1.9 eV) with increasing thickness from (368- 631 nm),This behavior is caused by the existence of allowed levels near the conduction band caused by structural defects inside the film, which mix with the conduction band levels and reduce the band gap in films. Electrical I-V investigations revealed a straight linear relationship between voltage and current, indicating the appearance of ohmic contact as a result of the alignment impact of the contact's work function. Also, as the intensity of light increases, the resistance decreases, resulting infree electron-gap pairs that contribute to current production, and the decrease in resistivity is due to the increase in conductivity. Furthermore, as the thickness of the CdSe thin film increases, so does its photosensitivity. Finally, the optical and electrical characteristics of the ITO/CdSe/Ag junction show that it may be used as; photosensors, part of a solar cell, and other optoelectronic applications.

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