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Effect of Ytterbium Nanosandwiching on The Physical Prosperities CdS thin films

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Declaration

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To My Loved Parents

Acknowledgments

First of all, I praise God for giving me the opportunity and the ability to fulfill this thesis as it is now. This work is recorded in my single name not one else, but in fact, it's a accomplished in combination with the dedicated work of other people, and today it is my turn to thank them all.

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Abstract

In this study, the effects of the sandwiching of a 70 nm thick ytterbium film between two layers of CdS on the structural, compositional, optical and electrical properties are investigated. The X-ray diffraction, scanning electron microscopy, energy dispersion X-ray, visible light spectroscopy and electrical-temperature techniques are employed to achieve these effects. It was observed that, the nanosandwiching of Yb between two 500 nm thick films of CdS enhances the crystalline nature of the films without altering the lattice parameters. Particularly, the grain size is increased by 25%, the strain, the defect density and the stacking faults are reduced by 31.5%, 43.7% and 25%, respectively. Optically, the Yb nanosandwiching is observed to enhance the visible light absorbability by at least 2.7 times of the whole range and by 8 times at 1.64 eV. The enhancement of the absorbability is associated with shrinking in the band gap and more interband states. In addition, an increase in the real part of the dielectric constant by 54% is observed when Yb was nanosandwiched in the CdS structure. The modeling of the imaginary part allowed exploring the electron-plasmon interaction parameters. A remarkable increase in the drift mobility from 281 to 996 cm²/Vs associated with plasmon frequency enhancement from 0.84 to 1.38 GHz was determined upon Yb nanosandwiching.

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Chapter One Introduction and Literature Survey

In recent years, the nanosandwich technique has become brighter as it revealed novel features presented by photoresponse and enhanced absorbability. Researches in the field of photovoltaic and solar cell fabrication has shown the potential to improve light absorption in thin solid film solar cells through using surface texturing and nanostructure coating techniques [1]. The nanosandwiching technique succeed in fabrication of nanocapacitors that have the feature measuring the charging time constants of materials in a non-destructive fashion without the requirement to connect wires or contacts [2]. In addition, the metal-dielectric-metal nanosandwich grating structure was observed to achieve extraordinary optical transmission performances at normal incidence in the ultraviolet-visible-near infrared regions [3]. When this structure was compared to other grating structures with single metal over layer, it reveals a wider band-stop characteristics and higher broadband transmission in the ultraviolet-visible region of wavebands. This design is reported to gain importance as it can be employed for developing high-performance subwavelength multifunctional integrated optical devices [3]. Moreover, it was reported that metallic nanoparticles can perform as label-free nanosensors that can monitor the local dielectric environment in their close vicinity [4].

In this study we have selected the CdS owing to its photovoltaic properties. It has been used as optical window with 80% transparency to design CdS/CdTe solar cells [5]. The thin films of cadmium sulfide which were grown on different graphene substrates by chemical bath deposition method were observed to exhibit shorter transient response time and higher photocurrent values [6]. In general, the structure of Cadmium Sulfide is hexagonal or cubic. It exhibits n-type conductivity with direct band gap of 2.42 eV

at room temperature [7]. The CdS thin films are prepared using many different techniques like screen printing [8], vacuum evaporation [9], electron beam evaporation method [10] and chemical bath deposition [11]. The CdS is a direct gap semiconductor with the smallest energy gap at the center of the Brillouin zone. The top most of the valence band is split due to crystal field and spin-orbit coupling into three spin degenerate states. Thus exciton states formed with holes in these valence band states reveals three energy bands denoted as A, B and C excitons [12]. The bands have energy band gaps of 2.482, 2.496 and 2.555 eV, respectively. In addition, CdS exhibits electron and hole effective masses of $0.25m_0$ and $0.71m_0$, respectively [12]. The melting temperature of this material is $1405 \,^{\circ}$ C at pressure of 3.8 atm. In addition, it is reported to exhibit intrinsic conductivity value of 2.81×10^{-2} (ohm.cm)⁻¹. The electron mobility in CdS crystal is very large $10^4 \, \text{cm}^2/\text{Vs}$ [12].

In light of the above mentioned properties here, in this thesis, we have selected the nanosandwiching of CdS to improve its features for possible uses in optoelectronic device fabrication. The thesis will focus on the structural properties to investigate the momentum confinements of the incident photons upon the surface of this material. The optical performance will be investigated in details as it is the most important feature of this material. Moreover, the electrical resistivity lowering through the control of the position of the Fermi levels will be considered in details.

In chapter Two, the theoretical background is discussed for all basics theories used and mentioned in the thesis. An X-Ray diffraction, braggs law and sherrer equation, the interaction of light with matter and Tauc equation were discussed. Moreover the current transport mechanisms were discussed which include themoionic emission and hopping conducting.

Chapter three discusses the experiments used in thesis to get the results. The evaporation technique was discussed in details to get the required thin films, the XRD, SEM and EDX are used to study the structure, composition and morphology. The UV-Vis spectroscopy was also used to study the optical properties, the current – temperature technique is used to study the dielectric conductivity, the hot probe method used to determine the type of the film.

In chapter four an investigation of characteristic of CdS and Yb nanosanwiched CdS is investigated in detail. Starting from the peaks observed in the XRD spectrum, we determine the average crystal size, strain, dislocation density, stacking factor and mismatch. From the optical study, the transmittance, reflectance and absorbance were characterized in details, then the energy band gap where determined. The real and imaginary parts of dielectric constant were investigated. The temperature dependent of electrical conductivity were studied and the current transport mechanism in the films were also determined.

Chapter Two Theoretical Background

This chapter reviews the background information and concepts which are mentioned through the thesis including some basics in X-ray diffraction. In addition, the interaction of light with material is characterized with some relations that describe it. Moreover Drude-Lorentz model, thermoionic emission and the current transport in semiconductor are discussed in details.

2.1 X-ray diffraction (XRD):

X-ray diffraction was used to identify the crystal structures and phase compositions of the samples. It is based on constructive interference of monochromatic X-ray radiations and a crystalline sample, when an incident ray interacts with atoms in the plane (hkl) a constructive interference occurred when the difference in path length between a and b is an integer number of wavelengths [13] as shown in fig.2.1 this principle which is known as Bragg's law is expressed mathematically by:

$$n\lambda = 2d\,\sin\theta\tag{2.1}$$

Where d the lattice inter-planar spacing of the crystal, θ is the x-ray incidence angle known as Bragg angle and λ is the wavelength of the characteristic x-ray.

This process relates the wavelength of electromagnetic radiation with the diffraction angle and the lattice spacing in the crystal [14].



Fig. 2.1: The geometry of Bragg's law

2.1.1 Scherrer equation:

Scherrer equation was developed in 1918 and used to evaluate the crystal size and the microstrain according to the broadening of the diffraction beam, given by the equation:

$$\beta \cos\theta = \frac{K\lambda}{D} + 4\varepsilon \sin\theta \tag{2.2}$$

Where, D is the average crystal size, and β is the full width at half maximum (FWHM) in radians, K is a constant related to the crystalline shape and equal 0.94, θ is the Bragg angle in radians and ϵ is the strain. This relation is applicable to grains less than 0.2 µm and provides information on crystal structural parameters such as phase, preferred crystal orientation (texture), and other structural parameters, such as average grain size, crystallinity, strain, and crystal defects. [15].

2.2 Optical properties

We consider the light as electromagnetic waves, when light falls on the surface of thin film, the photons will interact with the atoms (electron or hole) on the surface and induces small oscillations. As a result, these atoms radiate a secondary waves randomly in all directions, these waves gives the specular reflectance (R) which is detected by the device. If the total intensity is I_o , so $(I_o - R)$ intensity continue in the sample, when the photon gives all it is energy to the atoms, the absorbance (A) phenomena occurs. However, some incident light with specific energy can pass through thin layers without interaction, this part ensures the transparency (T) of thin film materials. Also a very small part of light is scattered and can't be collected by detector.

The total intensity of the incident light interact with material is equal to sum of the absorbed, reflected, transmitted and scattered intensities [16]. Hence, the total intensity of light can be written as:

$$I_o = I_T + I_R + I_A + I_s (2.3)$$

The absorbed fraction of beam is related to the thickness of the materials (d) and the manner in which the photons interact with the material's structure according to Bouguer's law:

$$I = I_o \exp(-\alpha d) \tag{2.4}$$

From the absorption coefficient (α) the energy band gap (Eg) can be determined according to Tauc equation [17].

$$(\alpha E)^p = \mathcal{C}(E - E_g) \tag{2.5}$$

Where C is constant related to transition, E is the light incident energy, and p is an index that represent the optical absorption process which is equal to 2 for indirect

allowed transition, 1/2 for direct allowed transition, 3 for indirect forbidden transition and 3/2 for direct forbidden transition.

In order to derive Tauc equation, we start with general expression for the asorption coefficient $\boldsymbol{\alpha}$

$$\alpha = \frac{(\hbar w)(transition \ probability \ /volume \ time)}{total \ intensity}$$
(2.6)

$$\alpha = \frac{(\hbar w)(P_{i \to f})}{I} \tag{2.7}$$

To solve the equation, we need an expression for $(P_{i \to f})$ and *I*.

 $(P_{i \to f})$ is quantum mechanical transition rate from initial to final state, defined by golden rule.

$$(P_{i \to f}) = \frac{2\pi}{\hbar} \left| M_{if} \right|^2 \rho \left(\hbar w \right)$$
(2.8)

Where ρ ($\hbar w$) is the density of final states and M_{if} is a matrix element describing the effect of external perturbation which couples the initial and final states defined as:

$$M_{if} = \frac{e}{m_o} \vec{A} \cdot \vec{p} \tag{2.9}$$

With m_o the mass of free electrons, p the electron momentum defined as $\vec{p} = i\hbar\partial$ and A is the vector potential of the incident field and expressed as

$$A(r,t) = A_o(expi(k.r - wt)), \qquad (2.10)$$

Where A_o is the initial potential at t=0, while the exponential is the Taylor expansion which is ignored when $A=A_o$ in the electric dipole approximation ([k.r]term is very small ~ 10⁻³), so the interaction Hamiltonian simplifies to;

$$M_{if} \approx er. \varepsilon_{photon}.$$
 (2.11)

Where, r is the electron position vector, er is the electron dipole moment (*pe*), and ε_{photon} is the amplitude of the light. According to the dipole approximation the electric field of light wave is equal to:

$$\varepsilon_{photon} = iwA_o. \tag{2.12}$$

The interaction Hamiltonian and the wave functions of the initial (ψ_i) and final (ψ_f) states must be known in order to describe the perturbation of the system due to the light irradiance.

$$\psi_i(r) = \frac{1}{\sqrt{V}} u_i(r) e^{ik_i \cdot r}, \qquad (2.13)$$

$$\psi_f(r) = \frac{1}{\sqrt{V}} u_i(r) e^{ik_f \cdot r}, \tag{2.14}$$

Where u_i and u_f are the envelope wave functions for the initials and final states, respectively, V is the volume normalization, and k_i and k_f are the wave vectors for the initial and final electron states, respectively. Substituted the wave functions and the perturbation Hamiltonian into the matrix element, we get

$$M_{12} = \frac{e}{V} \int u_f(r) e^{ik_i \cdot r} (\varepsilon_{photon} \cdot er) u_i(r) e^{ik_i \cdot r} d^3 r.$$
(2.15)

The electric dipole moment of the transition (M_{12}) caused by light and is different for every material. With the interaction matrix solved, the remaining part of the quantum mechanical transition rate is $g(\hbar w)$ the density of states which is equal for a parabolic band as

$$g(\hbar w) = \frac{1}{2\pi^2} \left(\frac{2m^*}{\hbar^2}\right)^{3/2} E^{1/2}$$
(2.16)

With E is energy $((\hbar w)$ and m^{*} is the effective mass. The above equation evaluated at initial and final states to get the joint density of states. Assume a term based on conversation of energy which state as,

$$\hbar w = E_G + \frac{(\hbar k)^2}{2\mu}$$
(2.17)

Where E_G is the band gap energy and μ is the reduced electro- hole mass. Thus, for photon energies less than $\hbar w$, the density of states term is zero, and above $\hbar w$,

So $g(\hbar w)$, becomes

$$g(\hbar w) = \frac{1}{2\pi^2} \left(\frac{2\mu}{\hbar^2}\right)^{3/2} \left(\hbar w - E_G\right)^{1/2}$$
(2.18)

Now getting back to I

$$I = -\frac{c}{8\pi} \left| \vec{E}^2 \right| = \frac{c}{8\pi} \frac{w^2}{c^2} \left| \vec{A} \right|^2 = \frac{w^2}{8\pi c} \left| \vec{A} \right|^2$$
(2.19)

Rewrite α , we get;

$$\alpha = \frac{(\hbar w) \frac{1}{2\pi^2} (\frac{2\mu}{\hbar^2})^{3/2} (\hbar w - E_G)^{1/2}}{\frac{w^2}{8\pi c} |\vec{A}|^2}$$
(2.20)

Simplifying the equation and putting the constants into C

$$\alpha = c \frac{\left(\hbar w - E_G\right)^{1/2}}{\hbar w} \tag{2.21}$$

$$(\alpha\hbar w)^2 = c^2(\hbar w - E_G) \tag{2.22}$$

2.3 Drude-Lorentz Model:

The Drude model of electrical conduction was suggested in 1900 to describe dispersion interactions between atoms or molecules in metals. By treating conduction electrons as a three-dimensional free-electron gas is an application of kinetic theory and assuming that the motion of these carriers is subjected to an electronic damping force (Γ) of coefficient that is inversely proportional to the scattering time (τ). The Drude model cannot be used in semiconductors and was therefore modified by adding Lorentz model. The modified model assumes that the vibration of atoms in solids can be represented by a series of damping oscillators [18]. Using these models we are able to obtain numerical solutions for the Plasmon dispersion curve of the semiconductor and dielectric interface.

According to the generalized Drude-Lorentz model which connects the imaginary part of the dielectric constant and the frequency of the incident light. The permittivity of a material can be written as follows:

According to the generalized Drude theory, the permittivity of a material can be written as follows [19]:

$$\varepsilon_{im} = \sum_{i=1}^{K} \frac{w_{ei}^2 w}{\tau_i ((w_{ei}^2 - w^2)^2 + w^2 \tau_i^{-2})}$$
(2.23)

With the subscript i refer to relative peak and k the number of observed peaks.

 w_{pi} is the electron bounded plsmon frequency $\left(w_{pi} = \frac{\sqrt{4\pi ne^2}}{m^*}\right)$, τ is the electron scattering time, w the reduced resonant frequency and n is the electron density.

We will investigate how to derive the dielectric constant of Drude model. When bounded electrons interact with electromagnetic field, The electrons will oscillate around their equilibrium position. From Classical point of view, we could approximate the oscillations by a damped oscillator. These oscillation process will extract energy.

Newton's second law written as

$$mx'' = -\beta x' \cdot k_s x - eE_x, \tag{2.24}$$

Where $-eE_x$ is the driving force, $-k_s x$ is the spring force of the oscillation, and $-\beta x^{\prime}$ is the damping force. Because the electric field is harmonic $-eE_x = -eE_oe^{-iwt}$, we can write Newton's equation as

$$x'' + \gamma x' + w_o^2 x = -e \ E_o e^{-iwt} / m, \tag{2.25}$$

Where $\gamma = \beta/m$ is the damping factor and $w_o = \sqrt{k_s m}$ is the natural frequency. To get the solution, we assume

$$x(t) = Ae^{-iwt} (2.26)$$

Substituting the above equation into equation 1.2 and solve for A, we get

$$A = -\frac{eE_o}{m} \frac{1}{w_o^2 - w^2 - i\gamma w}$$
(2.27)

And

$$x(t) = \frac{e E_o}{m} \frac{e^{-iwt}}{w_o^2 - w^2 - i\gamma w}$$
(2.28)

The polarization of one oscillator given by P = e.x(t), while the total polarization per unit volume is

$$p = N_o ex = \frac{N_o e^2 E_o}{m} \frac{e^{-iwt}}{w_o^2 - w^2 - i\gamma w} = \frac{w_p^2}{w_o^2 - w^2 - i\gamma w} \varepsilon_o E$$
(2.29)

With
$$w_p^2 = \frac{N_o e^2}{m\varepsilon_o}$$
 (2.30)

The polarization is related to the electric field through the electrical permittivity,

$$p = \chi \varepsilon_o E \tag{2.31}$$

So we have

$$\chi = \frac{w_p^2}{w_o^2 - w^2 - i\gamma w}$$
(2.32)

The relative dielectric constant ($\varepsilon = \varepsilon_o \varepsilon_r$) is

$$\varepsilon_r = 1 + \chi = 1 + \frac{w_p^2}{w_o^2 - w^2 - i\gamma w}$$
(2.33)

2.4: Current transport mechanisms:

The identification of the conduction mechanism in thin films determines the response time and signal quality of any electronic device such as when the thin film used as photoactive coating in solar cells and as gates in metal oxide semiconductor field effect transistors (MOSFETS).

Many factors may influence the charge transport mechanism of thin films, the most important one is the crystalline structure, its type and density, the defect type and its distribution, as well as the electrode nature and operating temperature. It is important to note that one or more mechanisms may be found in the same structure, corresponding on the temperature measurements range used [20]

2.4.1 Thermoionic emission.

When a solid material is heated sufficiently, free electrons gain thermal kinetic energy and flow from the surface or over a potential-energy barrier if the thermal energy given to the carrier overcomes the work function of the material. The band conduction in solid materials is mainly dominated by thermal excitation of charge carriers. Over a wide temperature (T) range, the dependence of electrical conductivity (σ) on T mathematically follows the Arrhenius form:

$$\sigma = \sigma_o \exp(-E_\alpha/KT) \tag{2.34}$$

With σ_0 is the pre-exponential factor, E_{α} is the activation energy, K is Boltzmann Constant and T is the temperature in Kelvin. Where $E_{\alpha} = E_c - E_f$ The difference between the minimum conduction band (E_c) and the Fermi level (E_f).

The decrease in E_{α} (T) with decreasing T appears as a result of the multi-excitation through the localized states whose transition has an activation energy decreasing with temperature. The transition through these localized states includes the hopping transport of charge carriers over the energy barriers.

2.4.2 Hopping conduction:

The decrease of electrical conductivity with decreasing temperature is a result of the multi-excitation through the localized states. This transition has an activation energy that is decreases with temperature, corresponds to the hopping transport of charge carriers over the energy barriers.

The hopping conduction mechanism happens through unoccupied localized states near the Fermi level. If the localized states are distributed quasi continuously, the hopping conduction between two sites, whose energy difference (W) is small, will become most probable. The probability of hopping increases with a factor of $\exp(-W/_{KT})$. Thus, the charged particles hop to the most probable site. While the hopping conductivity is given by

$$\sigma = \sigma_o \exp\left(-\left(\frac{T_o}{T}\right)^{1/4}\right) \tag{2.35}$$

With T_o is the degree of disorder in temperature, and given by:

$$T_o = \frac{\lambda \gamma^3}{K_B N(E_f)} \tag{2.36}$$

Here, $N(E_f)$ is the density of localized states near the Fermi level, λ is a dimensionless constant based on percolation parameter and γ is the decay constant and equal to the inverse of localization length. In the hopping conduction, we can evaluate the average hopping distance (**R**) and the average hopping energy (**W**) with the help of following equations [21].

$$R = \left(\frac{9}{8\pi\gamma K_B T N(E_f)}\right)^{1/4}$$
(2.37)

and

$$W = \frac{3}{4\pi R^3 N(E_f)}.$$
 (2.38)

Chapter Three Experimental Details

In this chapter the fabrication of the sample, conditions, the experimental techniques and the instruments used for the characterization of structural, SEM, EDX, optical and thermal properties of the CdS thin film and Yb sandwichedwill discussed in details.

3.1 Cleaning the substrate:

The glass substrates are cleaned first by distilled water then by alcohol in order to remove all dust on the surface. Then the substrates immersed in alcohol and deposited into ultrasonic resonator in distilled water at 70°C for 40 minute.

3.2 Thin film preparation:

The thin films were grown by evaporation in a physical vapor deposition technique in a Norm 600 physical vapor deposition shown in Fig.3.1 at a vacuum pressure of 10^{-5} mbar. The cleaned glass substrates are seated on the metal plate above the source of material (item 2 in the photo) and a (0.2) g of CdS were weighted and put in the CdS boat (item 1). Then a (0.1) g of Ytterbium oxide (Yb₂O₃) was also weighted and used to evaporate ytterbium sheet. Numerous devices and complementary equipment, such as vacuum pumps, gas supplying bottles, valves, sensors, cooling circuits and process.



Fig. 3.1: The Norm 600 physical vapor deposition system

When the system closed and the air inside the chamber removed using vent valve then the device run and wait the pressure to reach 10 mbar and open the turbo pump, During this process the shutter (item 3) must still close to avoid any random deposition to reach a good evaporated films,

The process of deposition begin when the vacuum reaches 10^{-5} mbar or less in order to prevent collisions between atoms, the systems supplied with current in order to ionize the material in boat which increases gradually to reach suitable deposition condition. The shutter opened for ~ 5 minutes and the atoms travel to substrates then reclosed the shutter when the thickness monitor reads the desired thickness.

The thickness of the films is measured with the help of thickness monitor (item 4), this monitor uses a quartz crystal microbalance (QCM) work as a sensor that measures the deposition rate and the total thickness of thin films during deposition[23]

The resulting 500nm thickness CdS films were used as a substrates to deposit a 70nm thickenss of Yb but one of 500 nm CdS film were closed by Tin papers before Yb deposition. The grown CdS/Yb films and the CdS alone film were used as substrates for the deposition of CdS with 500 nm thickness to get two films, a bare CdS with 1000nm thickness and CdS/Yb/CdS sandwiched with thickness 1070 nm shown in Fig. 3.2.



Fig. 3.2: The geometrical design of CdS and CdS/Yb/CdS thin film.

3.3 The x-ray diffraction (XRD) measurements:

X-ray diffraction characterization for CdS and Yb sandwiched was carried out using the Miniflex 600 X-ray diffractometer, fig. 3.4, with Cu K α radiation, of λ =1.5405 Å and an applied voltage 40 KV and current15 mA. Scanned 2 theta range was 5-70° with step size of 0.1° and the scan rate was 5.0°/min. The analysis of the diffraction data was performed using TREOR-92 evaluation computer program.



Fig. 3.3: The Miniflex 600 X-ray diffractometer

The basic elements of the X- ray diffractometers are shown in the setup below are Xray tube (source of radiation), the filters which is a metallic sheets used to produce monochromatic radiation, where the collimater used to reduce the size of the beam and directed toward the sample. Moreover, a sample holder where the sample set and stabilized by clay, and the X-ray detector are shown in Fig. 3.4 [24].



Fig.3.4: Schematic for the X-ray Diffraction setup.

3.4 Scanning Electron Microscopy (SEM) measurements:

The morphology and composition of thin films were studied using scanning electron microscopy (SEM) with a Joel JSM 7600F instrument and the energy dispersion X-ray analyzer (EDX) which is attached to SEM system. Scanning electron microscopic produces images of a sample, by scanning the surface, by a focused beam of electrons accelerated by high voltage. When the electrons interact with atoms in thin film it will produce various signals which collected with suitable detector contains information about the film surface morphology and composition. The elemental and chemical analysis of thin film recorded by using of the energy-dispersive x-ray analyzer which connected to the SEM system [25].

3.5 Optical measurements:

The optical transmittance and reflectance were recorded in the incident light wavelength range of 300–1100 nm, with the help of an Thermoscientific Evolution 300 ultraviolet-visible light spectrophotometer with VEE MAX II (pike) variable-angle reflectometer, with variation angle in the range of 30°–80°. The collected data measured at normal incidence of light (15°) and manipulated by means of the VISION software.

UV-Visible light spectrometer uses a tungsten lamp for visible region and hydrogen or deuterium lamp for ultra-violet region, while a monochromatic also used to produce a beam of single wavelength.



Fig. 3.5: ultraviolet-visible light spectrophotometer

3.6 The electrical measurement:

The electrical conductivity and temperature dependent current-voltage characteristic were recorded by using Keithley 230, which programable as a voltage source and Keithley 485 picoammeter. A bar of copper metal surrounded by copper-nickel wire which has low resistivity work as heater for the sample which stand on a holder connected with the copper bar n-type, a thermocouple connected with the sample in order to read the temperature.

Electrical contacts were obtained by vacuum evaporation of gold at the edge of the films by using prope mask. Then copper wires were indium-soldered to the contact areas. The ohmic nature of the contacts was confirmed by current–voltage (I–V) characteristics, which were found to be linear



Fig. 3.6 The setup of temperature dependent of electrical conductivit

3.7 Hot probe experiment:

The Hot-Probe technique is a conventional experiment that determines the conductivity type of semiconductors with help of hot probe with temperature $\sim 450 \,\text{C}^\circ$ and a standard multimeter. In this technique a hot probe is connected to the positive terminal of the multimeter while the cold probe connected to the negative, and both probes save attached to the semiconductor surface. If the multimeter reads out positive voltage then the semiconductor is an n-type, while p-type if the voltage negative.

As an explanation for this experiment when the probe attached the surface, thermally excited majority free charged carriers are diffused within the semiconductor from the hot to the cold probe. These translated majority carriers define the electrical potential sign in the multimeter. Thus, the hot probe surrounding region becomes charged with minority carriers while cold probe remains neutral [26].



Fig. 3.7: The set-up of the "hot-probe" experiment

Chapter Four Result and Discussion

In this chapter, the design, measurements, analysis and interpretation of the results will be considered. Particularly, we will focus on the growth, structural, optical and electrical properties of CdS/Yb/CdS films. The observed experimental data will be subjected to a modeling procedures to derive the related physical parameters.

4.1 Structural Analysis:

The structural characterization, the crystallographic properties, the compositional and morphological analysis of CdS and Yb nanosandwiched thin films were investigated using XRD, EDX and SEM techniques. The XRD patterns for CdS and Yb nanosandwiched CdS are presented in Fig. 4.1. CdS thin film displays a mean peak at 2θ =27.0°. Other minor peaks with low intensity appeared at 24.4°, 25.3°, 28.7°, 39.6° and 44.2°. These peaks confirm the polycrystalline nature of CdS.

The XRD data were analyzed by the "TREOR 92" software package and then compared with the results in the literature.

The calculated unit cell parameters referred to hexagonal structure of CdS [27] with lattice constant values of a = 4.12 and c = 6.68 A° obtained from the "TREOR 92" software package. As may be also seen from Fig. 4.1, the highest peak is oriented along the (002) direction, the crystal structure preferred plane orientation are consistent with these prepared by mechanical alloying using a planetary ball mill [28].

On the other hand, the XRD of CdS/Yb/CdS illustrated diffraction peaks at 2θ equal 24.3°, 25.3°, 26.9°, 28.6°, and 44.2° with maximum peak at 2θ =26.9°. Since the values are very closed to those of pure CdS, the same structure is assumed.



Fig. 4.1: The XRD spectrum of CdS and CdS/Yb/CdS

Even though the Yb sheet inserted between two CdS layers doesn't change the structure, the maximum peak becomes narrower and more intensive (inset of fig 4.1). No peaks that may correspond to Yb were detected in the XRD pattern this indicates that the inserted of Yb $^{+3}$ ions in CdS doesn't affect the crystal structure.

There are many possibilities that may be affected by the Yb⁺³ incorporation into the host CdS lattice: Yb⁺³ ions may occupy interstitial position, fill empty locations of Cd⁺² ions or replace Cd⁺² ions. Because the ionic radius of Yb⁺³ is smaller than Cd⁺² and the two ions are positive so the bonding between Cd⁺² and S⁻² is possible, thus the doped Yb atoms may be probably substitute in the site of Cd atoms forming the Yb₂S₃ compound as invisible minor phase in the structure of CdS [28].

Using the highest two maximum peaks which are oriented in the (002) and (100) direction respectively, and from the inter-planar spacing (d) which was calculated from

braggs law and tabulated in table 4.1, the crystal lattice parameters (a, c) of the hexagonal phase structure was determined according to the equation of d spacing for hexagonal [29] structure.

$$\frac{1}{d^2} = \frac{4}{3} \frac{h^2 + K^2 + hK}{a^2} + \frac{l^2}{c^2}$$
(4.39)

The values of a and c were found to be 4.062 and 6.600 A°, and 4.078, 6.624 A° for CdS and Yb sandwiched CdS respectively. These values are in good agreement with literature data with a = 4.14 A°, c= 6.72 A° that are reported for CdS prepared by hydrothermal method and agrees well with the software package predictions [30].

To investigate the structural properties associated with nanosandwiching of 70 nm thick Yb film in CdS, the average crystal size, the strain, the dislocation density and the stacking faults were calculated and listeded in Table 4.1. The average crystal size (D) and the strain (ϵ) were modified by using scherrer equation (2.2). The calculated values of grain size and microstrain for the pure CdS was found to be 21 nm and 7.3x10⁻³. The nanosandwiching of Yb increased the grain size value to 28 nm and decreased the strain value to 5.5x10⁻³. Since the strain is a reason for imperfection like vacancies, site-disorder, residual internal stress and dislocation [31], so less value of strain and larger value of grains mean better crystallization of thin film.

Other important parameters that can be calculated are the dislocation density (defects) (δ) and the stacking faults percentage (SF). δ is a measure of the number of dislocation in a unit area of a polycrystalline structure that is related to the strain in the lattice through the equation in a- direction [31]:

$$\delta = \frac{15\varepsilon}{aD} \tag{4.40}$$

Which is equal 12.58 and 7.08 in a-direction and equal 7.74 and 4.36 in c- direction for both pure and Yb nanosandwiched CdS, respectively.

The stacking faults represent the type of planar defects. It describes the disordering of crystallographic planes, and can be calculated using the relation [31]:

$$SF = \frac{2\pi^2 \beta}{45\sqrt{3} \tan\theta} \tag{4.41}$$

The calculated values of δ and SF% are displayed in Table 4.1. In addition to the presented data of table 4.1, it is beneficial to find the values of the lattice mismatch between the CdS and Yb layers.

The lattice mismatches (Δ %) between CdS and Yb along a-axis and c-axis are calculated using equation [31]:

$$\Delta\% = \frac{a_{CdS} - a_{Yb}}{a_{CdS}} \tag{4.42}$$

Where a_{CdS} is the calculated lattice constant of CdS and a_{Yb} the lattice constant of Yb and equal 5.487 A°. The lattice mismatches are found to be 36% and 17% along a and c axis respectively.

A close look on table 4.1 and with the result that the nanosandwiching of 70 nm Yb slab into the layers of CdS lead to a slight extension in the lattice constant along both axis, larger grain size, less strain, less stacking faults and less defect density. The substitution of some Yb atoms in vacant sites of Cd may be a reason for the reduction of defect density and reduction of stacking faults as well. However, the increase of the grain size should be assigned to reasons other than the extension in the lattice constant because the change in the lattice constant values are $\sim 1\%$ only, while the increase in the grain size reaches 25%.

Parameter	symbol	CdS	CdS/Yb/CdS
Maximum angle	heta (rad)	0.236	0.235
Intensity	I (a.u.)	1067	1200
FWHM	<i>B (rad)</i> x10 ⁻³	0.007	0.005
Grain size	D (nm)	21.33	28.44
Lattice spacing	d (nm)	0.331	0.331
Plane direction	Hkl	(002)	(002)
Strain	Е х10 -3	7.3	5.5
Stacking faults	SF %	0.360	0.271
Dislocation density	δ (x10 ¹² line/cm ²)	1.189	0.671
Lattice parameter	a (nm)	0.406	0.408
Lattice parameter	c (nm)	0.660	0.662

Table 4.1: The structural parameters of CdS and CdS/Yb/CdS thin films.



4.2 Morphology and composition

Fig. 4.2 The SEM and EDX for CdS and CdS/Yb/CdS films

Fig. 2 (a) and (b) represent the scanning electron microscope images for the nonsandwiched and the Yb nanosandwiched CdS, respectively. The images which represent a magnification of 120,000 times of the original scanned region show an approximately spherical shaped grains. The image of Fig. 2 (a), represents on the average three types of grains being distinguished in accordance with their sizes. More than 50 % of the scanned images indicate grains of average size of ~20 nm (shown as dashed circle of blue color). Another group which are shown by red dashed circles in the image of Fig. 2 (a) represent ~30% of average size of 27 nm. The remaining which are more bright and shown by solid dark circle are of average size of 41 nm. On the other hand, the image of Fig. 2 (b) displayed more homogenous distribution of the grains. In general, the average grain size is ~ 25 nm. The values detected from both images are close to those predicted by the X-ray diffraction technique.

To reveal information about the elemental distribution in the films, the energy dispersion of the X-ray was recorded and analyzed. The resulting spectra are shown in Fig. 2 (c) and (d) for the pure and Yb nanosandwiched CdS films, respectively. The spectra of the EDS reflect the peaks of the glass and the films. The normalized calculations for the atomic content of the Cd and S elements reveal a $Cd_{47}S_{53}$ before and after the nanosandwiching of Yb. The compositional analysis indicate physical nature of growth of CdS even in the presence of the Yb. The existence of Yb atoms in the structure of CdS is also confirmed from the strong peaks that are shown in Fig. 2 (d). Assuming that all the apparent elements other than Cd, S and Yb are related to the glass, then the Yb will reserve ~ 9% of the total volume of the CdS. Excluding the glass, the elemental distribution which is shown in the inset of Fig. 2 (d) indicate 43%, 48% and 9% for Cd, S and Yb, respectively.

From chemical point of view, since the ionic radius of Yb⁺³ is 87 pm [32] and that of Cd^{+2} is 96 pm [33], it is possible for the Yb⁺³ ion to replace the vacant sites of Cd⁺² and form Yb₂S₃ bonds. The formation of this bond would acquire more sulfur atoms because the Yb⁺³ ion (acceptor impurity) provide an extra hole due to its deficiency in valence electrons. The corporation of the extra hole to the structure of CdS explains the reason for the excess S (48%) atoms over those of Cd (43%). However, because the ratio of the atomic contents of the Cd to that of S are 0.87 and 0.90 before and after the nanosandwiching of Yb, respectively, and because the X-ray patterns did not display intensive peak that relate to the Yb₂S₃, it is possible to accept that the CdS/Yb/CdS sandwiched structure is mostly of physical type (substitutional and/or interstitial).

With these features, the Yb film can be mostly regarded as a metallic slab being inserted between two layers of CdS. Generally, The cadmium vacancies and interstitial sulfur are reported to act as acceptors, while sulfur vacancies and interstitial cadmium act as donors [33]. Since in accordance with the EDS data the CdS have excess S over Cd before and after the addition of Yb, then the CdS should exhibit n-type of conductivity, even in the presence of Yb.

Even though there exist excess sulfur as seen from the EDS, The samples are of n-type conductivity found by hot probe technique. The conductivity type of CdS is normally n-type some Cd interstitial atoms. The Cd atoms take interstitial positions due to lack of sulfur. In the presence of Yb ions at substitutional positions of Cd without sorming the Yb₂S₃ compound as minor phase (not observed in XRD). Then, assuming charge neutrality, in accordance with the formula $Cd^{+2}{}_{1-x}Yb^{+3}S^{-2}$ with x being the number of electrons needed to compensate the charges. Then such substitution introduce x e`s in the conduction band causing the n-type conductivity. In case of interstitial position, the Yb⁺³ in CdS matrix can be presented by $Cd^{+2}{}_{x}Yb^{+3}S^{-2}$. This introduce 3x electrons into the conduction band causing the n-type conductivity. In addition sulfur vacancy also introduce e`s according to $Cd^{+2}S^{-2}{}_{-\delta}$, where δ is the number of electrons in the conduction band, forming the observed n-type conductivity.

The Yb metal is one of the F_{m-3m} space group and exhibit a cubic closed backed crystal structure of lattice parameter of 5.487 °A which indicates a lattice mismatch of ~35% and 17% along a and c- axes respectively. Although large lattice mismatched heterojunctions causes high efficiencies in solar energy conversions, it may lead to relaxation via the generation of dislocations. The formation of such dislocations that behave as minority carrier recombination centers which lowers the efficiencies [34] of photovoltaic materials is reduced by the nanosandwiching of Yb between layers of CdS.

Studies on the effect of Ga-doping and Ga-K-co-doping on the structural and compositional properties of these thin films have shown that an increased level of K in Ga-doped CdS samples causes a degradation in the crystal quality. EDS results have shown that the best stoichiometric film is acquired when K content is 2 at% in Gadoped CdS films. The grain size also slightly increased upon incorporation of K atoms in the host structure [35]. Further increase in the K atomic content decreased the grain size of CdS, the behavior is assigned to increase in the nucleation density at the initial stage of the film growth. In another study, the Zn doping into the structure of CdS is observed to decrease the lattice parameters of the hexagonal structure [36]. The effect was attributed to the Zn^{+2} ionic substitution in sites of Cd^{+2} . Deep studies on the structural analysis assign the grain growth to the completeness of the recovery and recrystallization processes. When these two processes are complete no further reduction in the internal energy of the grains is possible. Thus, the total energy stabilization is realized by the reduction the total area of the grain boundaries [37]. The reduction in the grain boundaries can also be observed from the SEM images which are displayed in Fig. 1 (a) and (b). The grains of the CdS/Yb/CdS appear closer to each other than those of pure CdS. Meanwhile, during the recovery process, the deformed grains reduce their stored energy by the removal or rearrangement of defects in their polycrystalline structure. As Table 1 displayed, the defect density is significantly reduced from 1.19×10^{12} lines/cm² to 6.7×10^{11} lines/cm² reduced by the insertion of 50 nm thick Yb layer [38].

4.3 Optical Measurements:

An investigation of the optical parameters such as transmittance (T), reflectance (R) and absorbance (A) provide a complete picture for band structure and energy band gap of thin films as will be shown in this section. The transmittance and reflectance data were recorded with the help of UV-Vis spectrometer for as grown CdS and Yb nanosandwiching thin films in the incident photon wavelength in the range 300-1100 nm.

As shown from Fig. 4.2(a) the as grown CdS thin film has a large transmission in a wide range of light spectrum and reaches a maximum value of ~90% at $\lambda = 750$ nm indicating its applicability in optoelctronic devices such as solar cell window layers [39]. For the sandwiched structure the transmittance is reduced compared to that of CdS. The maximum transmittance (70%) is observed at $\lambda = 910$ nm. The transmittance spectra of two films show a sharp absorption edge at 480 nm and 500 nm for CdS and CdS/Yb/CdS respectively. The decrease in T% values in the presence of Yb is due to the high reflectivities of Yb metal.

On the other hand the reflectance spectra shown in Fig. 4.2(b) exhibit an interesting features represented by peaks at wavelengths 540 nm and 570 nm with maximum values of 25.5% and 33.4% for the as grown and Yb nanosandwiched CdS respectively. The R spectrum decrease and reach minimum values of 5% at λ =740 nm for CdS and 2.5% at λ =910 nm for Yb sandwiched CdS. The reflectance spectrum of Yb nanosandwiched was shifted towards the infrared region.

To get more accurate information about the dynamic of light in the films, the absorbance was calculated by the relation = 1 - T - R, where E is the extinction of light and equal (scattered + absorbed light). The absorption spectra is shown in Fig.

4.2(c). Yb slab enhances the absorbability of CdS, which increase the ability to capture the incident photon energy and be applicable in optoelectronic devices. However, the as grown CdS and Yb nanosandwiched films show a sharp decrease in the absorption at~ 500 nm and reach minimum values ~ 5% and 30% for CdS and Yb nanosandwiched respectively. Then, the spectrum of CdS exhibits a small increase reaching 11% while the absorbance of the Yb nanosandwichd sample nearly remains constant. The absorbance spectrum of films didn't reach the zero value which indicate the formation of interband transitions in CdS and CdS/Yb/CdS films.

The formation of the interbands in the energy band gap of CdS by the Yb atoms is probably due to the interaction between the f^{14} states of Yb with the energy band states of CdS. The interband transition relates to the electron scattering at interfaces and electron –phonon interactions [37].



Fig.4.2 (a)-(c): The transmittance, reflectance and absorbance spectrum for CdS and CdS/Yb/CdS, respectively in the range of 300-1100 nm.

To have more information about the absorption and study the effect of Yb layer on the optical properties of CdS, the absorption ratio is calculated. Fig. 4.3 illustrates the absorption ratio of the nanosandwiched thin film to bare CdS ($R_{\alpha} = \frac{A_{cds/Yb/cds}\%}{A_{cds}\%}$). It is observed from the curve that R_{α} increases with increasing the energy until energy value of 1.7 eV is reached. It then decreases with increasing photon energy. So the effect of thin layer of Yb between two layer of CdS increase the absorbability of CdS by 8 times at 1.7 eV in the visible region.



Fig.4.3: the absorbability of Yb in CdS

The absorption coefficient (α) was calculated according to the relation: $\alpha = A/d$ [37], Where d is the film thickness. The relation between the absorption coefficient and the photon energy is presented in Fig. 4.4. The spectrum shows three regions of variation. The weak absorption tail which should be related to the defects and impurities of thin film. The sharp increasing region (above 2.0 eV) is obvious and reach a maximum

values at 2.7 eV. The remaining part of spectrum (above 2.5 eV) remains constant which means that the films reach a light saturation so any energetic photons reflected through the film doesn't affect the absorption.



Fig. 4.4: The absorption coefficient of CdS and CdS/Yb/CdS thin films.

From the high absorption region, the energy band gap (E_g) can be determined using Tauc equation (2.5)

From the plot of $(\alpha E)^{1/p}$ -E, the appropriate value of p is determined by choosing the most linear plot while the value of E_g determined from the intercept with the E-axis. In more details, $(\alpha E)^{1/2}$, $(\alpha E)^2$, $(\alpha E)^{1/3}$, $(\alpha E)^{2/3}$ are plotted as a function of photon energy and shown in Fig. 4.5 (a)-(d). As clear from the graphs, the fit that include the widest range of points is observed for p =1/2. Thus the direct allowed electronic transitions are dominant in CdS. The energy band gap values for CdS and Yb nanosandwiched films as illustrated in Fig. 4.6 (a) are equal to 2.41 eV and 2.33 eV, respectively. The



value of energy gap of CdS is close to the calculated value of CdS technique about 2.36 eV [38].

Fig. 4.5: The (αE)1/p – E variation for CdS and CdS/Yb/CdS thin films for p = 2, 1/2, 3 and 3/2 respectively.



Fig. 4.6 : The energy band gap of CdS and CdS/Yb/CdS.

The existence of energy gap in CdS is related to the crystal field anisotropy and spin orbit interactions [39]. While the difference in energy band gaps upon Yb nnosandwiching are $\Delta E = 0.08$ eV.

In contrast to the results observed in this work which indicated shrinkage in the band gap as a result of Yb nanosandwiching, a widening in the optical bandgap was reported for Mg, Cl and K-dopings [40,41]. Owing to the Burstien effect , the Mg and Cl dopings resulted in a blueshift of the band gap from 2.46 to 2.73 eV [40]. An energy band gap value of 2.45 eV for 3 at%-5 at%. K -dopings and value of 2.43 eV for Ga-doped CdS thin films are also mentioned [40]. As the grain size increased, excluding the quantum size effect, the authors assigned the widening in the band gap to the increase in the internal pressure associated with the occupation of the K atoms of interstitial positions

in the lattice which may result in an increase in the strain. A widening in the energy band gap from 2.36 to 2.45 eV was also observed via the Zn doping in CdS [42]. On the other hand, Cu doped CdS thin films are reported to exhibit a shrinkage in the energy band gap value associated with annealing in the air at 250 and 350 °C. The shrinkage in the band gap was assigned to the improved crystallinity [43] and due to the formation of band tails that may result from the oxidation process. In the scope of these observations and with reference to our X-ray data analysis which indicated crystallinity enhancement via Yb nanosandwiching, the shrinkage in the band gap may be attributed to the enhanced crystallinity presented by larger grain sizes, less strain and less dislocation density and stacking faults that arises from the metal induced crystallization process.

4-4 Dielectric properties:

To investigate the practical applications possibilities of the structures and the effect of insertion of Yb between two CdS layers, we attempt to study the dielectric constant which related to the optical data Fig.4.2. The effective dielectric constant (ε_{eff}), $\varepsilon_{eff} = \varepsilon_r + i\varepsilon_{im}$, can be determined from the equation [44]:

$$R = \frac{(\sqrt{\varepsilon_{eff}} - 1)^2 + k^2}{(\sqrt{\varepsilon_{eff}} + 1)^2 + k^2}$$
(4.43)

Where, k is the extinction coefficient and equal $\alpha\lambda/_{4\pi}$

The effective dielectric constant reveals the real (ε_r) and imaginary (ε_{im}) parts which are shown in Fig. 4.8 and Fig. 4.9, by the help of the relations $\varepsilon_r = \varepsilon_{eff} - k^2$ and $\varepsilon_{im} = 2\sqrt{\varepsilon_{eff}}k$, respectively. As shown in Fig. 4.8, the real part of dielectric constant for Yb nanosandwiched film is higher than pure CdS. Both spectra slightly increase with increasing freqency and reach the maximum peaks at 555 THz (2.30 eV) and 526 THz (2.18 eV) for CdS and Yb nnosandwiching respectively. Then sharply decreased and remain constant in the range (600-1000)THz. These peaks are less than the value of the energy band gap that calclated in the optics part.

It is clear from the figure that the higher value of the real part of the dielectric constant of nanosandwiched films is related to the existence of Yb layer which supplies more surface charges that couple with S⁻² holes or ion cores [45]. While there apppear no effect of Yb on the value of the dielectric force above 650THz, ε_r highly enhanced from 9 to 14 by Yb nanosandwiching. However, in the high frequency range (750-1000 THz) dielectric constant (~4.5) is weakly responding to the presence of the Yb in the CdS.



Fig. 4.8: The real dielectric constant for CdS and CdS/Yb/CdS in the range of 300-1000 THz $\,$

Since the dielectric resonance peaks appeared at an energy lower than that of the energy band gap, it should be assigned to other reasons. Reports which concern the sulfur vacancies in CdS observed this green band at 2.27 eV and assign it to the sulfur vacancies. The oscillation is believed to occur due to the transitions near the bottom of the conduction band and the top of the valence band and recombination between donor-acceptor pairs as long as second ionization states of sulfur vacancies dominates [46]. The shift in the position of the dielectric resonance peak upon doping was also assigned to the reduction in the recombination rate. The filling of the sulfur vacancies with donor atoms decreases the recombination rate by forming the electron-hole pairs. For our case the samples contain excess sulfur. The excess sulfur is also reported to form donor levels in the band gap of CdS which in turn supports the transitions from these sites [46]. Another reason for the presence of the dielectric resonance peak at 2.27 eV could be the reservation of the S vacant sites by unpurposely present oxygen atoms [47].

On the other hand, the imaginary part of the dielectric spectra, shown in Fig. 4.9, are show small decreased followed by increased when increasing frequency from 300 THz to reach the maximm value at 640 THz and 530 THz for CdS and Yb nanosandwiched respectively, then the spectrm slightly decrease with increase frequency in the remaining range. The ε_{im} spectra are also red shifted



Fig. 4.9: The imaginary dielectric constant for CdS and CdS/Yb/CdS in the range of 300-1000 THz

As the imaginary part of the dielectric constant is directly proportional to the optical conductivity. The presence of the Yb in the structure of CdS necessarily indicates the improvement in the conduction parameters. For this reason, and according to the Drude - Lorentz model which connects the relations between the imaginary part of the dielectric constant and the frequency of the incident light and expressed by the relation (2.28) the imaginary part of the dielectric constant was analyzed.

From these Drude parameters we can calculate the frequency independent drift mobility $(\mu = e^{\tau}/m^*)$ with m^* is the effective mass of Free electrons, where $m^* = 0.11m_e = ((2m_{cds}^*)^{-1} + (m_{Yb}^*)^{-1})^{-1}$ with $m_{Yb}^* = 1.00m_e$ [49] and $m_{cds}^* = 0.25 m_e$ [50]. The results of the solution of the above equation are tabulated in Table 4.2. and shown by black line in Fig. 4.9

	CdS				CdS/	Yb/Cd	S	
i	1	2	3	4	1	2	3	4
$ au_i(\mathrm{fs})$	1.10	0.50	045	0.40	0.84	0.65	0.35	0.24
$W_{ei}(\mathrm{x}10^{15}\mathrm{Hz})$	4.00	1.50	0.45	0.34	6.30	1.10	0.50	0.30
$n(X10^{17} \text{cm}^{-3})$	1.50	4.00	4.70	6.00	1.45	3.10	4.10	6.00
μ (cm ² /Vs)	281	7.00	4.90	13.3	996	174	79.0	47.0
W _{pei} (GHz)	0.84	0.98	2.31	3.36	1.38	1.29	2.18	3.78

Table 4.2: The fitting parameters for the CdS and CdS/Yb/CdS nanosandwiched films in accordance with Drude-Lorentz model

The tabulated data indicates that the electronic friction damping term ($\gamma = 1/\tau_i$), and $\gamma_{CdS} = 0.9$ and $\gamma_{CdS/Yb/CdS} = 1.25$. Yb⁺³ increased the damping force in the electrnic media for the most dominant oscillator (i = 1). This caused a shift with electron frequency from 4.0×10^{15} to 6.3×10^{15} Hz. At the same time due to the contribution of the valance electrons shared by Yb atoms to the valance band of CdS the free electron density decreased from 1.5 to 1.45 cm⁻³.

Even though the number of free electrons increases the electrical conductivity $(\sigma = ne\mu)$. It also increased the drift mobility from 281 to 996 cm²/V.s, the value of the drift mobility is remarkable and comparable to those determined from Hall Effect measurements for pure CdS thin films [51, 52]. Literature data reported value of 344 cm²/Vs for CdS thin films of thickness of 200 nm [52]. Low values of 2-12 cm²/Vs are also reported for a free carrier concentration of 10¹³- 10¹⁸ cm⁻³ in CdS films [53]. The improvement in the mobility values were assigned to the carrier concentration

variation which is believed to be associated with the concentration of defects arising from sulfur vacancies and/or cadmium interstitials in the CdS films [53]. Thus, the insertion of the Yb into the structure of CdS is also able to enhance the drift mobility of free carriers owing to its ability of increasing the grain size, decreasing the grain boundary and reducing the defect density as observed from the X-ray analysis. It is also may relate to decrease the collision between carriers which result an increase the drift speed then increasing the mobility.

The dielectric loss as a function of frequency is a ratio of the imaginary permittivity to real permittivity, shown in Fig. 4.10. Generally the less tangent values are lower for the pure CdS samples than for CdS/Yb/CdS. The shape of variation of the loss tangent spectra is the same for both samples. The larger values of the loss tangent for the CdS/Yb/CdS over CdS is assigned to the contribution of the Yb which enhances the optical conductivity.

It is also noticable that for F < 550 THz (4.26 eV), while the loss tangent values weakly repond to the decreasing signal frequency in CdS, it sharply increases when Yb is sandwiched between two layers of CdS.



Fig. 4.10 Dielectric loss of CdS and CdS/Yb/CdS, as a function of frequency

3.4. Electrical transport properties

The electrical conduction plays an important role in the performance of the semiconductor devices. In order to investigate the current transport mechanism, the temperature dependent electrical conductivity of CdS and Yb nanosandwiched were measurement in the temperature range of 300-400 K as shown in fig. 4.11.

It is obvious from the figure that the electrical conductivity is increased with increasing temperature over the all studied range for CdS, while the spectrum of CdS/Yb/CdS thin film shows a steady increase of conductivity with increasing temperature until 385 K then a small decreasing trend appears. The conuctivity of Yb sandwiched CdS is higher than pure CdS. This difference is related to the increase in the carrier concentration due to substitutional incorporation of Yb ions in the CdS structure, also the increase of

conductivity can be attributed to the excess of Cd atoms and S deficiencies as we have observed in the EDS analysis rise of carriers due to sulfur deficiencies, which agrees with the compositional analysis [51].



Fig. 4.11: The temperature dependence of electrical conductivity of CdS and Yb sandwiched thin films.

In order to investigate the current transport mechanisms in the films, we first plot a graph between $(\ln(\sigma) - \frac{1000}{T})$ as shown in fig. 2.12 in accordance with equation (2.12) which can be rewritten as $(ln(\sigma) = ln(\sigma_o) - \frac{E_{\alpha}}{KT})$. The conductivity activation energy is determined from the slope and found to be 387 meV for bare CdS and 176 meV for CdS/Yb/CdS. To express that the thermoionic emission of charged carriers is the dominant transport mechanism in the samples, the conductivity activation energy must be larger than kT which is equal 25.7 meV at room temperature, so this transition is valid in both films.

The values of the conductivity activation energy being less than $E_g/_2$ means that the samples are of extrinsic type semiconductors. As the samples were found to be n-type then the activation energies being 387 and 176 meV should refer to two donor states one is formed by unintentionally existing impurities in the undoped CdS (387 meV) and the other is formed by the presence of Yb atoms.

However, since the Yb doped samples contain shallower donor level, the observation of donor level in CdS was not possible through measuring the conductivity of CdS/Yb/CdS films.

The high value of the activation energy indicate that the most probable current conduction mechanism is the thermionic emission of charge particles over the grain boundaries. Since the resistance of the grains is much less than that arises from the boundaries, then the boundaries are regarded as the main reason.



Fig. 4.12: The variation of $\ln(\sigma)$ as a function of T^{-1} for CdS and CdS/Yb/CdS thin films.

For low temperature measurements, it is reported that there is a dc hopping conduction which may dominate. To check the existence of this conduction mechanism in the samples a graph between $\ln(\sigma) - T^{-1/4}$ was plotted. From the slope the hopping parameters were determined, the degree of disorder (T_o), then from the calculated T_o and according to the equations (2.36)-(2.38) the localized states near the Fermi level, the average hopping energy (W) and the average hopping distance(R) are calculated.



Fig. 4.13: The plots of $ln(\sigma)$ versus T^{-0.25} for CdS and CdS/Yb/CdS samples

In accordance with the variable range hopping theory, this mechanism is valid only when $T_0 > 10^3$ (K), W > KT and $(\frac{R}{\xi}) >> 1$, where ξ is the localization length and equal 10°A [46]. By consider this conditions and check the value in table (4.3) the variable range hopping should valid again in two samples at low temperature < 350K. However, because the hopping energy is very large compared to the standard values [46], then the domination of hopping transport is still in question. The standard value of degree of disorder is ~ 10^4 - 10^5 in polycrystalline systems and 10^6 - 10^8 in amorphous systems as the tabulated value is 10^9 , then in accordance with these values the fims should be amorphous which is inconsistent with our observation, for this reason we shall continue thinking that the most preferable current transport mechanisims is the thermoionic transition mechanism.

Reconsidering that, the thermoionic transition mechanism is the only mechnisim, then because the addition of the Yb shifts the donor level closer to the conduction band of CdS. The shift in the donors level as a result of Yb nanosandwiching could be due to the more free carriers contributions from the Yb metal to the conduction band of CdS and due to the *f*-orbital's energy bands overlapping with those of CdS. The electronic configuration of Cd, S and Yb are $4d^{10}5s^2$, $3s^23p^4$ and $4f^{14}6s^2$, respectively. Since the *f*-orbitals are at higher energy levels than those of Cd, the Yb make stronger bonding and the overlapping of the energy levels make it easier for the electrons to move freely in the material, thus, the resistivity to the electronic motion is reduced.

	Ea (meV)	$T_0(K)$	$\mathbf{N}(\mathbf{E}_{\mathbf{f}}) \left(eV^{-1}cm^{-3} \right)$	R (cm)	W (eV)
CdS	387	1.91x10 ⁹	8.81x10 ¹⁷	9.43x10 ⁻⁷	0.323
CdS/Yb/CdS	176	3.82x10 ⁷	4.40×10^{19}	3.55x10 ⁻⁷	0.122

Table 4.3: The current transport mechanisms parameters:

Chapter Five Conclusions

In this thesis, we have discussed the possibility of the formation of new nanosandwiched structure for the purpose of modification of the physical properties of the CdS photo sensitive material. The deposition of a 70 nm thick Yb film between two films of CdS was observed to significantly alter the physical properties. Particularly, The structural and morphological analysis clearly displayed better crystallinity presented by larger grain size and less defects density, as well as reduced stacking faults between planes. In addition, a wider range of light absorption was covered upon the Yb sharing. The enhanced absorbability was associated with narrowing in the energy band gap. The structural and the optical modifications we found to be the sensor that control the behavior of the dielectric spectra. The modeling of the imaginary part of the dielectric constant for pure and Yb nanosandwiched samples, revealed higher optical conductivity, high drift mobility and large scattering time at femto second level.

On the other hand, the electrical conductivity measurements in the temperature range of 300-400 K have shown a semiconductivity property of the samples. The conductivity of the Yb doped sample in higher than that of not sandwiched ones. The behavior is assigned to the closer donor level formed by Yb atoms compared to the pure ones. Still it is worthy of consideration that the nanosandwiching procedure need more focus to control the chemical interactions of the interfaces and to adopt the conductivity measurements, more adequately.

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Conferences

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اثار زراعة رقائق اليتيربيوم النانومترية على الخصائص الفيزيائية لرقائق الكادميوم سالفيد

الملخص

في هذه الاطروحة؛ تم استكشاف اثار حشو فيلم اليتيربيوم بسمك ٢٠ نانوميتر بين طبقتين من الكادميوم سالفيد على الخصائص البنيوية، التركبية، الضوئية والكهربائية . وقد تم توظيف حيود الاشعة السينية، المسح الالكتروني المجهري، تشتت الاشعة السينية ، التحليل الطبقي والتقنية الكهربائية – الحرارية في در اسة هذه التاثيرات. لقد تم ملاحظة ان حشو اليتيربيوم بن طبقتين رقيقتين بسمك ٢٠٠ ناتوميتر من الكادميوم سالفيد يعزز الطبيعة البلورية ملاحظة ان حشو اليتيربيوم بن طبقتين بسمك ٢٠٠ ناتوميتر من الكادميوم سالفيد يعزز الطبيعة البلورية ملاحظة ان حشو اليتيربيوم بن طبقتين رقيقتين بنسمك ٢٠٠ ناتوميتر من الكادميوم سالفيد يعزز الطبيعة البلورية للافلام بدون تغيير الثوابت البنيوية لها. على وجه الخصوص تم زيادة حجم الجزيئات داخل الفيلم بنسبة ٢٢%، ما للافلام بدون تغيير الثوابت البنيوية لها. على وجه الخصوص تم زيادة حجم الجزيئات داخل الفيلم بنسبة ٢٥%، لافلام بدون تغيير الثوابت البنيوية لها. على وجه الخصوص تم زيادة حجم الجزيئات داخل الفيلم بنسبة ٢٥%، لافلام بدون تغيير الثوابت البنيوية لها. على وجه الخصوص تم زيادة حجم الجزيئات داخل الفيلم بنسبة ٢٥%، للافلام بدون تغيير الثوابت البنيوية لها. على وجه الخصوص تم زيادة حجم الجزيئات داخل الفيلم بنسبة ٢٥%، لافلام بدون تغيير الثوابت البنيوية لها. على وجه الحصوص تم زيادة حجم الجزيئات داخل الفيلم بنسبة ٢٢%، ما الحفو و ٢٥% على التوالي. ضوئيا لوحظ ان شطيرة اليتيربيوم عزز من امتصاص الضوء المرئي بنسبة ٢٢، مرات على الاقل على طول المدى و لوحظ ان شطبرة اليتيربيوم عزز من امتصاص الضوء المرئي بنسبة ٢٢، مرات على الاقل على طول المدى و الوحظ ان شطبرة اليتيربيوم مين رقائق الكادميوم سالفيد ، وير تبط تعزيز امتصاص الضوء مع متقلص فجوة الطاقة والتداخل بين المستويات . اضافة الى ذلك لوحظ زيادة في الجزء الحقيقي من ثابت الازلية بنسبة ٢٠% على طول المدى و اليتيربيوم بين رقائق الكادميوم سالفيد ، وسمحت عمل نموذج حاسوبي الجزء الخيالي باستكشاف معاملات تفاعل اليتيربيوم بين رقائق الكادميوم سالفيد ، وسمحت عمل نموذج حاسوبي الجزء الخيالي باستكشاف معاملات تفاعل اليتيربيوم من ما ٢٨ الى ٢٩٦