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Preparation And Optical Characterization Of CdSe Thin Films With Different Thicknesses Using Thermal Evaporation

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ABSTRACT

In this study, CdSe thin films with different thicknesses (300–900 nm) were prepared using the thermal evaporation technique. Structural and optical properties were investigated using X-ray diffraction (XRD), atomic force microscopy (AFM), and UV–Vis spectroscopy. XRD results confirmed a polycrystalline hexagonal structure with a preferred (002) orientation that became more pronounced with increasing thickness. Optical measurements revealed a direct band gap that decreased with increasing film thickness, accompanied by an increase in absorption coefficient in the visible region. AFM analysis showed improved surface morphology and increased grain size at higher thicknesses. These results indicate that CdSe thin films are promising candidates for optoelectronic and photovoltaic applications.

1. Introduction

Researchers have increased studies related to thin-film technology, due to its great importance in The areas of modern electronic industry, in addition to what has been mentioned, is the field of its use in the manufacture of solar cells Photovoltaic has multiple industrial uses, as it is included in the installation of electronic devices in the form of rectifiers, Capacitors, Transistors, etc., as well as electromagnetic wave detectors within specific spectral ranges. In addition, it has many other electronic and optical applications, including its use in the circuit industry Integrated electronic circuits and switches, photocopying and reproduction optical, and in the manufacture of ordinary and thermal mirrors and reflective and non-reflective coatings, and shall be approved This depends directly and mainly on the type of membrane used and the nature of the raw materials included in its composition crystal [1,2].

Cadmium selenide is known as an inorganic chemical compound Cadmium element compounds, its chemical formula is (CdSe) and it has a black color, and because it is related to one of the elements of the sixth group of the periodic table (Se), so it is considered a glass semiconductor galcogenate that belongs to the group (II- VI) of the periodic table [3,4].

APPLIED SCIENCE

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Vol. 2, No. 1, 2026, pp. 1-16

ISSN 3104-8935

Cadmium selenide crystallizes in two crystal systems, one of which is cubic (cubic), which appears in two phases, the first is called (rock-salt) and is symbolized by (α - CdSe), while the second phase is called (Sphalerite) and is similar to the composition of zinc sulfide (Zinc blende) and is symbolized by (β - CdSe), and the other system in which the compound crystallizes is the hexagonal system or what is called (Wurtzite) and is symbolized by (γ - CdSe). While the first system is unstable (Metastable state), and is specifically formed from electrochemical processes, the other system is thought to be the most stable crystal system and is directly formed either in an unstable manner by Cubic phase annealing process or directly by other methods of preparation [5-10].

Cadmium selenide has a high absorption coefficient value, especially within the visible region the electromagnetic spectrum, and because of this property, has received great interest in the field of solar cell industry as an electro-optical material, whether in its pure form (CdSe Pure) or in the form of layers (Multilayer's) [11-14].

The aim of this work is to investigate the effect of film thickness on the structural and optical properties of CdSe thin films prepared by thermal evaporation, with a focus on their suitability for optoelectronic applications.

Chalcogenide compound

A type of semiconductor consisting of the union of an element of a certain group with one of the elements of the group the sixth of the periodic table, which is (Se, Te, S) except for the element oxygen, and examples on that compound under the current study (CdSe), which belongs to the compounds of the group of elements Binary - hexagram (II-VI) of the periodic table, which in turn belong to galcogenate compounds, as well as compounds of the elements of the triple group - hexagram (III-VI) and elements the quaternary-hexagonal group (IV-VI) of the periodic table, as well as compounds of the elements of the pentagonal-hexagonal group (V-VI) of the periodic table also. [15,16]

Chalcogenate compounds are generally characterized by being transparent to visible and near-infrared rays, depending on the value of their energy gap. As for the ionic valence between the atoms of their elements, they can be divided on this basis into two parts: [15,16] :

1. Stoichiometric compound

Most of the binary systems of galcogenates are chemically equivalent, meaning that they possess a chemical equivalence between their positive and negative ionic atoms, for example compounds (CdTe), (CdSe), (ZnSe) and others.

2. This appears in the triple or quaternary systems consisting of more than one element in addition to the element galcogen, called galcopyrite, whose elements have different weight ratios. Where they are chemically inequivalent, meaning that they do not possess a chemical equivalence between their positive ionic atoms and negative.

Optical properties of semiconductor thin films

The optical properties of semiconductor films depend on the nature of the crystal structure of the material to be studied their properties, The process and conditions used to make thin films from them, along with the accompanying physical variables thickness changes, evaporation pressure, sedimentation rate, core temperature, annealing temperature, and doping, are all to blame for exposing the properties of semiconductor films (such as absorbance and transmittance), and any change in these factors causes a noticeably change in these properties, especially the deviation of the main absorption edge, which then results in the occurrence of a change in the value of the optical energy gap, as well as the absorption coefficient, the value of the energy gap, and the basic absorption edge (which, by studying it, can be identified the optical applications of the films prepared from these materials. [17,18]

Optical absorption

The interaction between the photons of the electromagnetic radiation projected on the material and the charges contained in that material (the electrons of its atoms or ions) is the main factor in the operation of most modern electronic devices, because the basic operating process in the light-emitting diode (LED) is the spontaneous emission as a result of the forward bias. In lasers, it is the stimulated emission, but in photodetectors and solar cells, the basic operating principle is absorption, It also serves as the foundation for earlier operations since it is based on the optical energy gap value of the semiconductor and the energy of the incident radiation photons [19].

The basic absorption edge is characterized as one of the most important characteristics of semiconductors that possess a forbidden energy gap, as it is one of the basic optical parameters, and it is necessary to study its location for any membrane prepared within the projected electromagnetic spectrum, because of the consequent importance in determining the location of the forbidden energy gap for a semi. The conductor and thus determine the nature of the application in which the prepared membrane material can be harnessed at its service, as well as it gives important information about the properties of the energy packages formed in the material and the type of electronic transitions that take place in it, and it can be defined as the region that represents the beginning of the electronic transition (the beginning of optical absorption) between the two beams Parity and conduction, and represent the lowest energy difference (E_g) between the highest point at the top of the parity beam (V.B) and the lowest point at the bottom of the conduction beam (C.B). It is equal to the quantity ($h\upsilon_o$) and as in equation (2-18), where it represents (υ_o) the threshold frequency of the beam The electromagnetic force required for the occurrence of electronic transition [20].

Absorbance is defined as the ratio between what a membrane absorbs of a given intensity (to the original intensity). For the electromagnetic radiation directed at it at a certain wavelength, The following connection describes the absorbance, which is often a quantity without units [21,22]:

$$\boldsymbol{A = \frac{I_A}{I_0}} \qquad (1)$$

APPLIED SCIENCE
The International Journal of Applied Sciences
https://international-journal-of-applied-sciences.jo
Vol. 2, No. 1, 2026, pp. 1-16
ISSN 3104-8935

Absorbance is associated with both transmittance and reflectivity by the following relationship:

$$A + T + R = 1 \qquad (2)$$

Where the relationship above is defined by the law of energy conservation, from which the values of reflectivity (R) can be found. Absorbance is also associated with transmittance by the following relationship from which the absorbance values of the prepared films were found:

$$A = \log\left(\frac{1}{T}\right) \qquad (3)$$

One of the fundamental optical parameters used to determine the kind of electronic transitions that take place in the semiconductor, whether direct or indirect, is the absorption coefficient, which is defined as the amount of attenuation in the radiation energy flux per unit distance in the direction of wave propagation inside the membrane and its units (cm^{-1}). It is given through the Lambert equation in absorption after its derivation and as follows [23,24]:

$$I = I_o\, e^{-\propto t} \qquad (4)$$

The transmittance values of the membranes are usually obtained either directly through the use of an optical spectrometer (UV-VIS 1800 spectrophotometer), This measures the transmittance in relation to wavelength between (300 to 1100 nm), or it is calculated by adopting the following relationship:

$$T = 10^{-A} \qquad (5)$$

And by rephrasing equation (5) above, we obtain the value of the absorption coefficient (α) mathematically through the following equation:

$$\propto = 2.303\,\frac{A}{t} \qquad (6)$$

Literature Survey

- Shiraki, et al, 2001[25] studied the effect of copper doping with a doping ratio of (3%) On the structural and optical properties of pure (CdSe) films prepared by thermal evaporation technique in V Vacuum and with different deposition temperatures (30, 100, 150, 200) °C. The results of the examinations showed. The composition showed that the compound material (CdSe) in its powder form had a multiple crystalline structure. The crystallization is of the hexagonal type, with atomic growth in several crystalline directions, the characteristic and prevailing of which were in the directions (100), (103) and (110), respectively.
- The researcher Bhuse, 2005 [26] prepared (CdSe) films by adopting the chemical bath deposition method, and then studied the effect of mercury doping with rates ranging

between (0.01-10) mol % on the structural, optical and electrical properties of the prepared films. The results of the study showed that the prepared films In both pure and doped forms, it had a polycrystalline crystalline structure with a clear increase in both the degree of crystallinity and the granular size resulting from the increase in the doping ratios. results of the visual examinations showed the value of the optical energy gap for the pure films was equal to (1.87eV) and thus stable at this value. Even the few doping ratios with a slight decrease appearing in the value of (E_g) at high doping ratios, as well as the results of the electrical tests showed that all the prepared films had electrical conductivity of the negative type (n-type) with a decrease in the electrical resistivity value with the increase in the doping ratios.

- Delekar, et al, 2014 [27] manufactured a hybrid junction of cadmium selenide thin films on silicon bases with a thickness of (840) nm, as well as preparing thin films on glass bases by adopting the chemical bath evaporation method, and then Structural, optical and electrical tests were carried out for all prepared samples. The results of the scanning electron microscope (SEM) showed that the prepared films were composed of small, regular spherical granules with a uniform spherical shape. As for the results of the structural tests, they showed the prepared films were polycrystalline and of the type cube.

Experimental

CdSe Alloy Preparation

In order to obtain an equivalent weight ratio of (50:50) for each of the elements cadmium (Cd) and selenium (Se) correspondingly (Se50 Cd50), the compound (CdSe) was synthesized from the German business (Fluka) with a purity of (99.999%), at a rate of (3gm) for the alloy as a whole. utilizing a four-digit sensitive electronic scale (Precisa). To prevent an explosion caused by the high vapor pressure of selenium, the equivalent weights for the aforementioned weight ratios, which are (1.762gm) and (1.238gm) for the elements cadmium and selenium, respectively, were put in a quartz glass tube with an inner diameter of (1.1cm) and a length of (35cm). After being thoroughly cleaned with water, liquid soap, and alcohol, it is tightly closed at one end with an oxy-acetylene torch, emptied of air using a rotary pump, and then placed in an electric oven to prepare for the burning process. Once the pressure inside it reaches (10=3 torr) limits, it is then sealed at the other end. When the temperature inside the furnace reached a temperature just above the compound's melting point (1260 °C), the glass sample was placed in an inclined position inside a (Carbolite) heating furnace to melt its constituent parts at a temperature gradient rate of (C/min ° 5). A residence time of three hours was calculated for the sample in accordance with the compound's phase diagram, while moving it occasionally to ensure homogeneity of the mixture during the melting process. It was then cooled using the slow cooling method for the melt, and the sample was broken to extract the compound's alloy from it, where the prepared alloy was subjected to tests X-ray diffraction to ensure that it is the required material, and then it was ground by means of a laboratory grinder (glass mortar) to obtain

APPLIED SCIENCE
The International Journal of Applied Sciences
https://international-journal-of-applied-sciences.jo
Vol. 2, No. 1, 2026, pp. 1-16
ISSN 3104-8935

the powder of the material to be ready for structural examinations 3- and to prepare films from it.

Preparation (CdSe) thin film

Pure (CdSe) films were prepared by placing the weights (0.6383 ± 0.0004 gm, 0.4965 0.2128, 0.3546), equivalent to each thickness under study (300,500,700) ± 20nm, respectively, in a (boat) of molybdenum metal, and after the pressure inside the evaporation chamber reached the amount(2.2 x 10^{-5} torr) was used using the E306 coating unit, which was supplied by (Edwords) company of (0.7±0.1) nm/sec and a (boat) is heated to the point of material evaporation by running a high continuous current via a current transformer designed for this purpose at room temperature (27 °C), and then the samples are allowed to cool within the evaporation chamber at next, it was prepared for the next step, which is measuring the thickness, and then conducting laboratory tests on it and studying its structural and optical properties. The thickness of the prepared films was measured using a reflective spectrophotometer, which depends on the principle of measuring the reflectivity spectrum of the prepared films as a function of wavelength within the range nm (450-750), where the results are represented graphically to obtain a chart representing the behavior of the material under examination within the aforementioned range. And by comparing the resulting values from the device with those stored in the device's memory and for a specific thickness of the material itself, which is called (Standard Thickness), and through the regression of the data obtained between the prepared and standard models using the (Fitting Measurement) function, the thickness of the prepared membrane is measured as well as the rest of the thickness. Other optical constants such as refractive index and inertia through a program designed for this purpose that comes attached to the aforementioned device as a CD, and it is worth noting that this method is more efficient and more accurate in measuring thickness compared to the gravimetric method. After preparing pure cadmium selenide films doped with tin with a doping ratio of (3%), the its optical properties using a UV-Visible 1800 Spectro Photometer, where the transmittance values were measured as a function of wavelength change within the range (1100-300 nm) and from the resulting transmittance spectrum, the reflectance and absorbance spectra were calculated, as well as the calculation and the value of the optical energy gap for all the prepared films (α), other optical constants such as the absorption coefficient (E_g).

X-Ray Diffraction Result Of CdSe Thin Films

The results of the X-ray diffraction tests revealed that all the prepared cadmium selenide films, which came in a variety of thicknesses and were either pure or doped with tin at a percentage doping level (dropping ratio 3%), had a polycrystalline crystalline structure and a hexagonal structure with atomic growth in three crystal directions: (002), (102), and (103). The majority of them are found in direction (002) and for all created films, which is compatible with research's findings [29]. Additionally, when comparing the results from the surface clearance (dhkl), crystal lattice constants (a, c), and crystal diffraction angles

Vol. 2, No. 1, 2026, pp. 1-16

(2Θ) corresponding to the positions of the distinctive peaks of the samples of pure films of various thicknesses with what came from the values contained in the card numbered (0459-08), the results were largely the same, as shown in table (1).

Table (1) The values of surface clearance, diffraction angles and crystal lattice constants for cadmium selenide (CdSe) films prepared with different thicknesses.

Thickness (nm)	(hkl) (JCPDs)	2Θ (JCPDs)	2Θ observed	d(A°) (JCPDs)	d(A°) observed	a,c (A°) (JCPDs)	a,c(A°) observed
300	(002)	25.3538	25.5008	3.5100	3.4902	4.299 7.010	4.333 6.980
	(102)	35.1072	35.2600	2.5540	2.5435		
	(103)	45.7884	45.8503	1.9800	1.9775		
500	(002)	25.3538	25.4436	3.5100	3.4980	4.299 7.010	4.298 6.996
	(102)	35.1072	35.1796	2.5540	2.5490		
	(103)	45.7884	45.8855	1.9800	1.9760		
700	(002)	25.3538	25.3227	3.5100	3.5143	4.299 7.010	4.283 7.029
	(102)	35.1072	Disappear	2.5540	Disappear		
	(103)	45.7884	45.7703	1.9800	1.9808		
900	(002)	25.3538	25.4389	3.5100	3.4985	4.299 7.010	4.286 6.997
	(102)	35.1072	Disappear	2.5540	Disappear		
	(103)	45.7884	45.9152	1.9800	1.9750		

It is also clear from the diffraction models of the pure films shown in figure (1) that there is a noticeable increase in the intensity reflected from the first peak with distinctive directionality (002) with an increasement in thickness of prepared film the atoms of the precipitated layers tend to arrange themselves in the direction with the lowest internal energy in order to get rid of their surplus energy and reach the stable state, and from the succession of the evaporated atoms by arranging themselves in that direction (002) - by increasing the thickness - it will become distinct and clear, while the two directions will start the other two decay and this a consistent with results of the Studies [30].

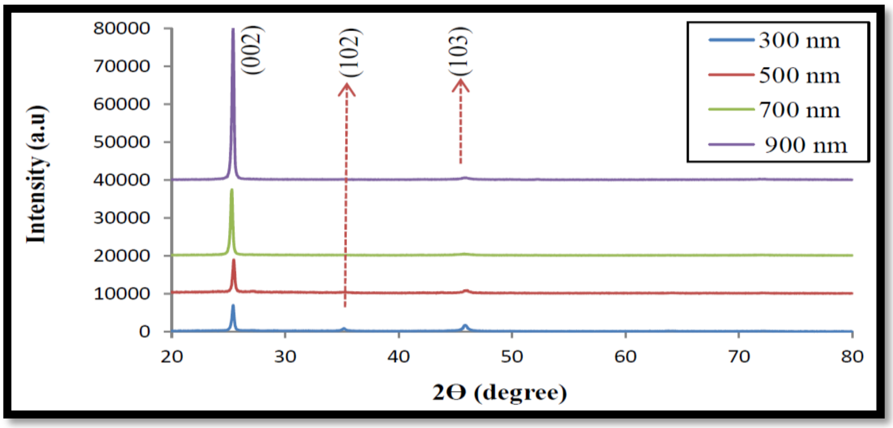
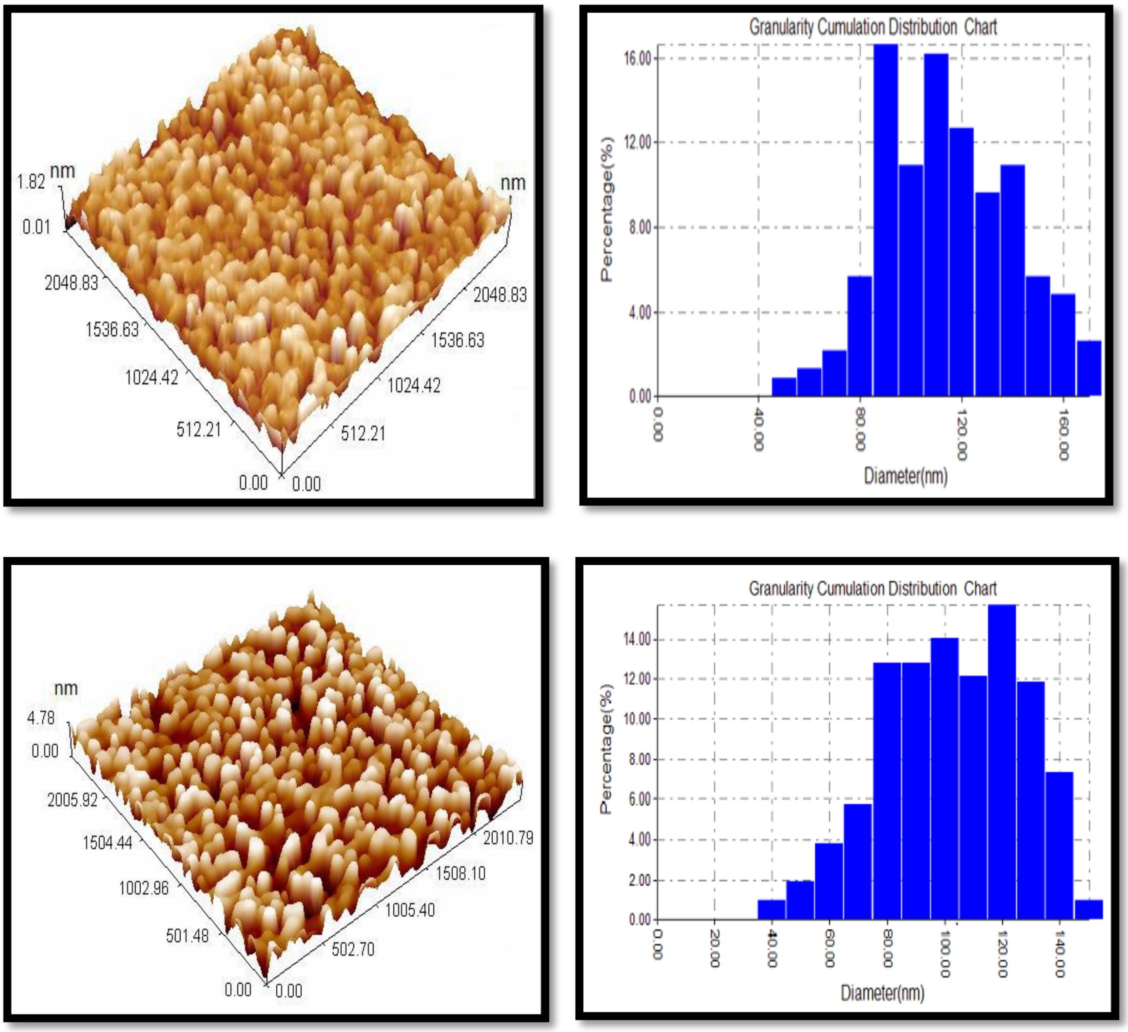


Figure (1) Model of pure cadmium selenide sheets made with various thicknesses using X-ray diffraction.

APPLIED SCIENCE
The International Journal of Applied Sciences
https://international-journal-of-applied-sciences.jo
Vol. 2, No. 1, 2026, pp. 1-16
ISSN 3104-8935

Figure (2) shows by atomic force microscopy (AFM) three-dimensional images of pure cadmium selenide films prepared with different thicknesses (300, 500, 700, 900) nm, with a scheme of the distribution of membrane granules over the examined surface area. The higher the thickness increases, as it becomes of a larger granular size with a uniform and homogeneous distribution along the surface area of the membrane, and the reason for this is attributed to the increase in the aggregation of the atoms of the material deposited on the surface with the increase in thickness (especially in the (002) direction) - to become larger clusters, including larger islands thus forming a homogeneous film with a larger granular size, thus improving its structural properties (especially the increase in its crystallinity) on the one hand, and thus increasing the surface roughness on the other hand. This is consistent with the results of X-ray diffraction assays.



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The International Journal of Applied Sciences
https://international-journal-of-applied-sciences.jo
Vol. 2, No. 1, 2026, pp. 1-16

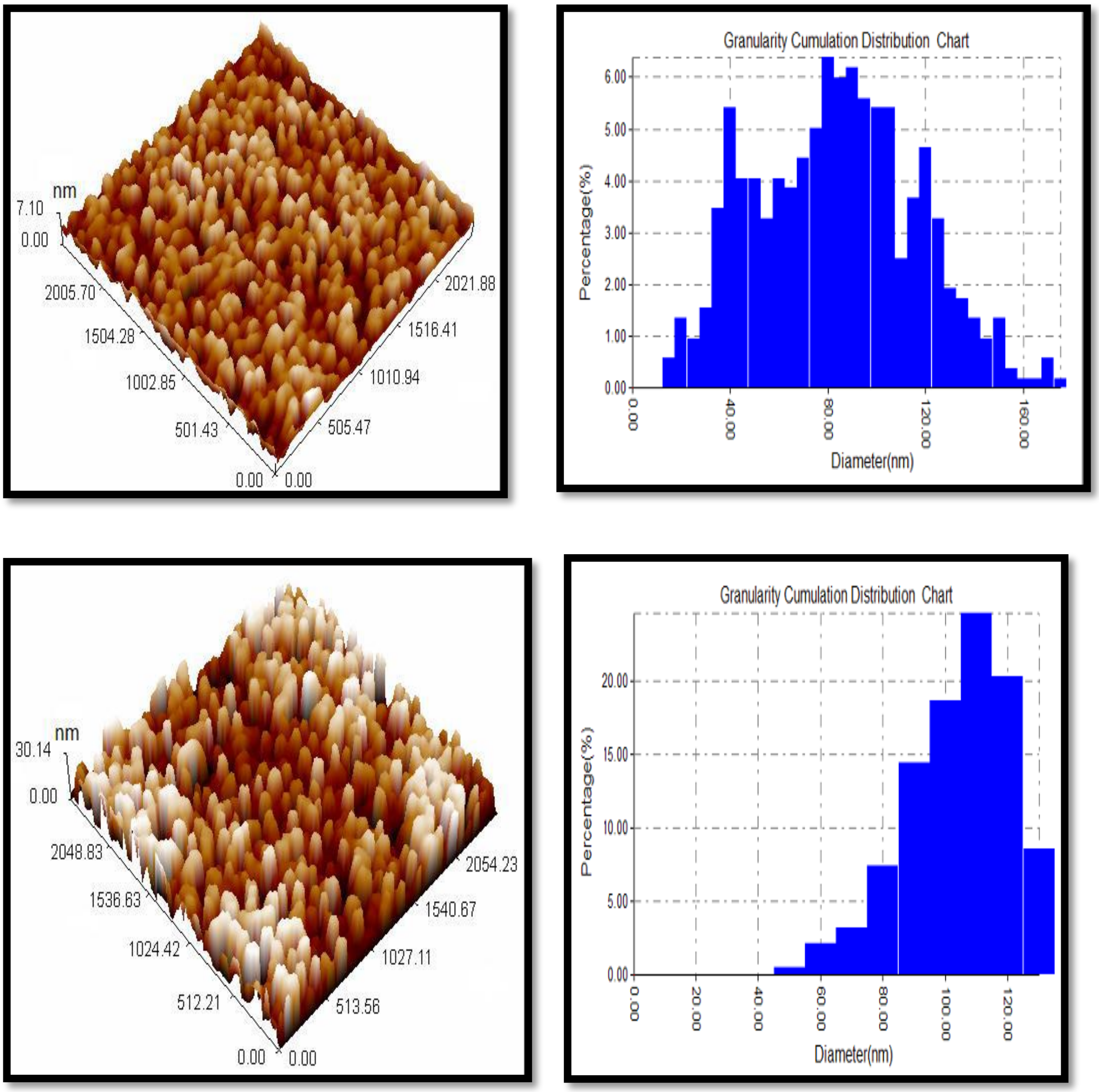

Figure (2) AFM images of pure CdSe films prepared with different thicknesses

Table (2) lists the average values for surface roughness, square root mean square roughness, and particle size for all pure cadmium selenide films made at various thicknesses. Its importance and improve the output of solar cells to be manufactured at the highest thickness of the record (900 nm).

Table (2) Average values of particle size, surface roughness, and square root mean square roughness for pure (CdSe) films prepared with different thicknesses

thickness(nm)	Grainsize(nm)	Rootmean square(nm)	Roughness Density(nm)
900	96.18	8.71	7.541
700	91.77	1.43	1.181

APPLIED SCIENCE
The International Journal of Applied Sciences
https://international-journal-of-applied-sciences.jo
Vol. 2, No. 1, 2026, pp. 1-16
ISSN 3104-8935

500	**80.96**	**1.17**	**0.978**
300	**78.81**	**0.25**	**0.197**

The change in the percentage absorbance spectrum for pure cadmium selenide films made at various thicknesses of 20 (300, 500, 700, 900) nm is shown in Figure 3 as a function of wavelength. The behavior of the produced films was investigated across the wavelength range of (300-1100) nm, as shown in figure (3). Any fried fish has an absorption spectrum that is most pronounced at short wavelengths (high photon energy), then narrows as it approaches long wavelengths. Its energy is equivalent to or greater than value of the forbidden energygap at any thickness record. The image also demonstrates how the absorption rises typically with the thickness of the produced film. This is because each Photon falling in surface of the prepared film will be subjected to multiple absorption processes by the crystals contained within each individual granule, increasing the degree of crystal lization of the prepared film and the ensuing increase in particle size.

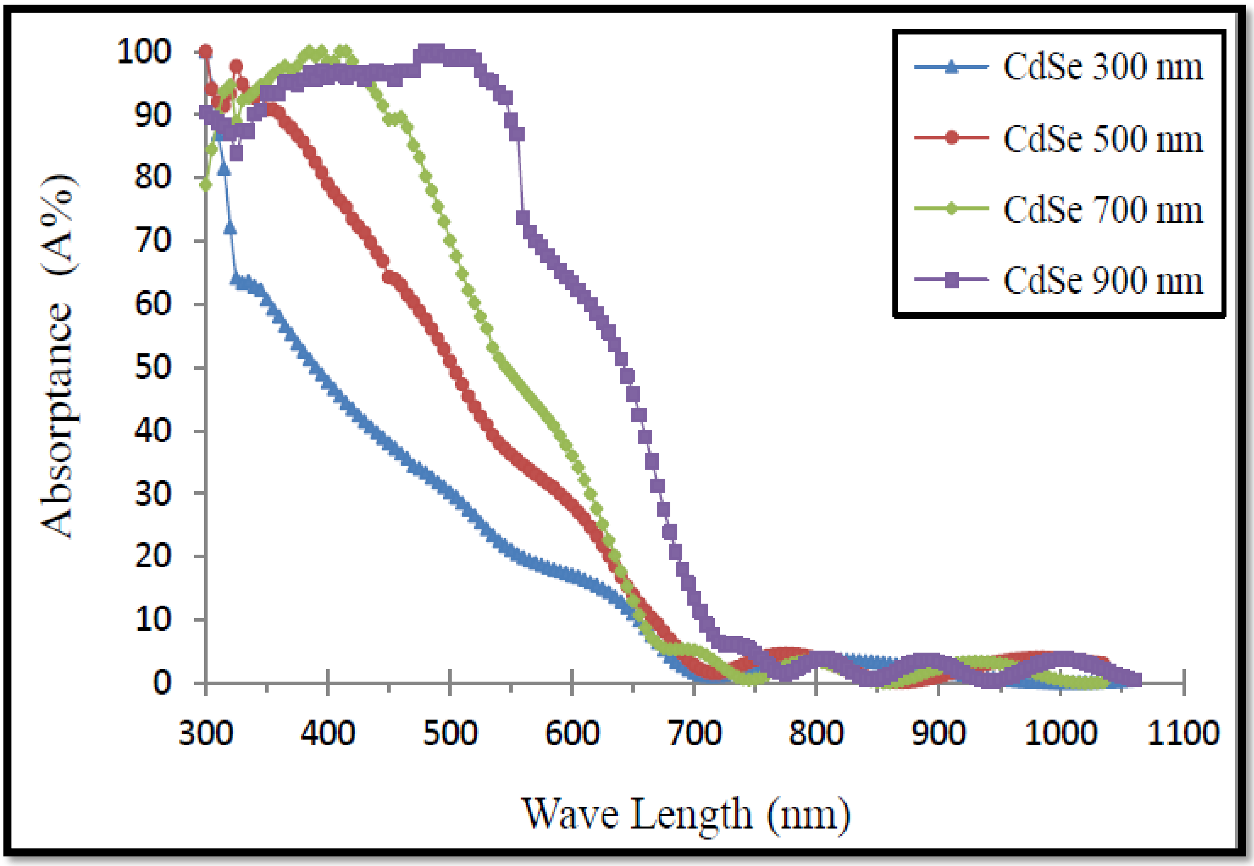

Figure (3) Variation of the % absorbance spectrum for (CdSe) films made with various thicknesses as a function of wavelength

Figure (4) displays the alteration in the transmittance spectrum of pure cadmium selenide films made with various thicknesses as a function of wavelength (300,500,700,900 nm) (±

20) and with a measurement range of (300-1100) nm, including the ultraviolet range (300-400) nm. The region demonstrates that the transmittance is consistent for all generated films, not surpassing (3%), which suggests that it may be possible to create a detector employing the prepared membrane material that operates within the range of the electromagnetic spectrum. The visible spectrum's short wavelengths are (400-620) nm; it is recognized from this range that the transmittance It is still very undervalued, especially for films manufactured with the highest prepared thickness (900nm), as its transmittance did not exceed (5%) at the time when the films prepared with the lowest thickness (300nm) recorded a percentage transmittance that did not exceed (30%). As for the remaining spectrum the visible region is (620-780) nm. It is noted that there is a sudden increase in the permeability of the films prepared in general, to reach its maximum value (90%) approximately for the films. With the lowest prepared thickness (300 nm), and less than that (60%) approximately for films with the highest prepared thickness (900 nm) infrared and near wavelengths longitudinal (780-1100) nm, The reason for this is attributed to Fluctuation of the bonds that occur between the Positive Cadmium Ions and the Negative Selenium ions as a result of energy, as is noted throughout this region that the spectrum of transmittance in it has a shape similar to that of a sine wave with the emergence of successive peaks and for each prepared thickness. Due to infrared radiation's inability (low energy) to dissolve the link between those ions, a hill of fringes is produced.

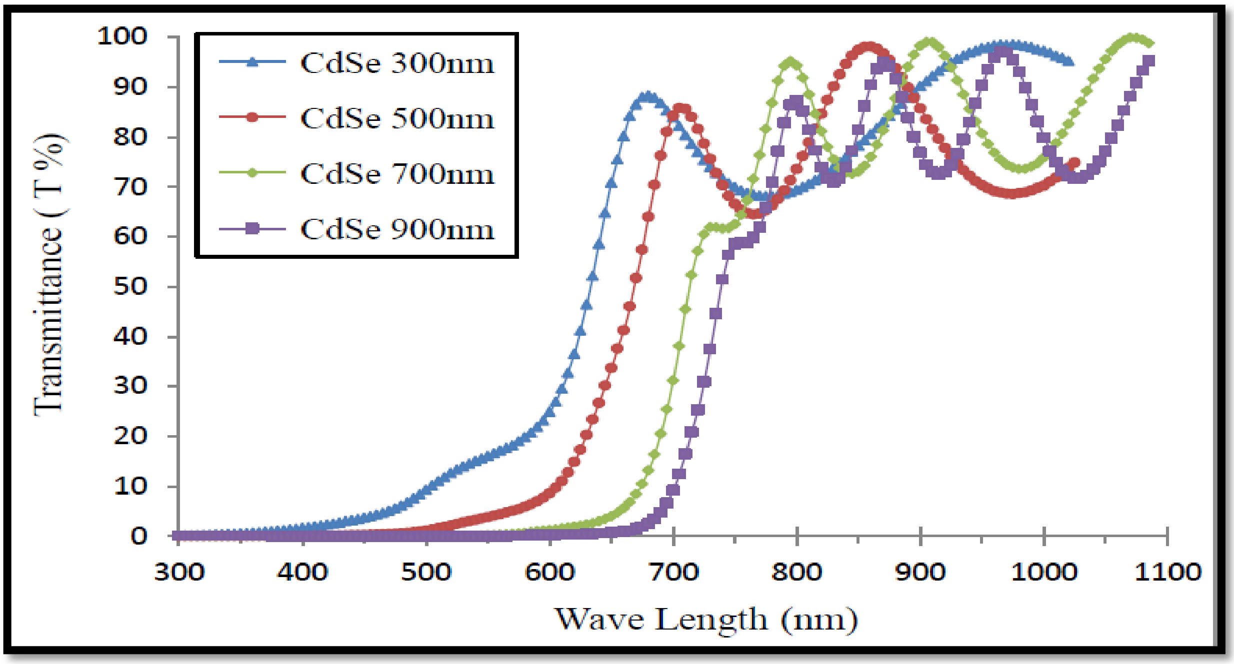

Figure (4) Variation in the % transmittance spectrum of the CdSe films made at various thicknesses as a function of wavelength.

Figure (5) shows the percent reflectance spectrum as a function of wavelength for pure (CdSe) films and prepared with various thicknesses. This is another indication that the membranes' roughness has increased with increasing thickness and agrees with the figure's

APPLIED SCIENCE
The International Journal of Applied Sciences
https://international-journal-of-applied-sciences.jo
Vol. 2, No. 1, 2026, pp. 1-16
ISSN 3104-8935

conclusion that the reflectivity of the membranes decreases with increasing thickness for the wavelength ranges located within the visible region of the electromagnetic spectrum.

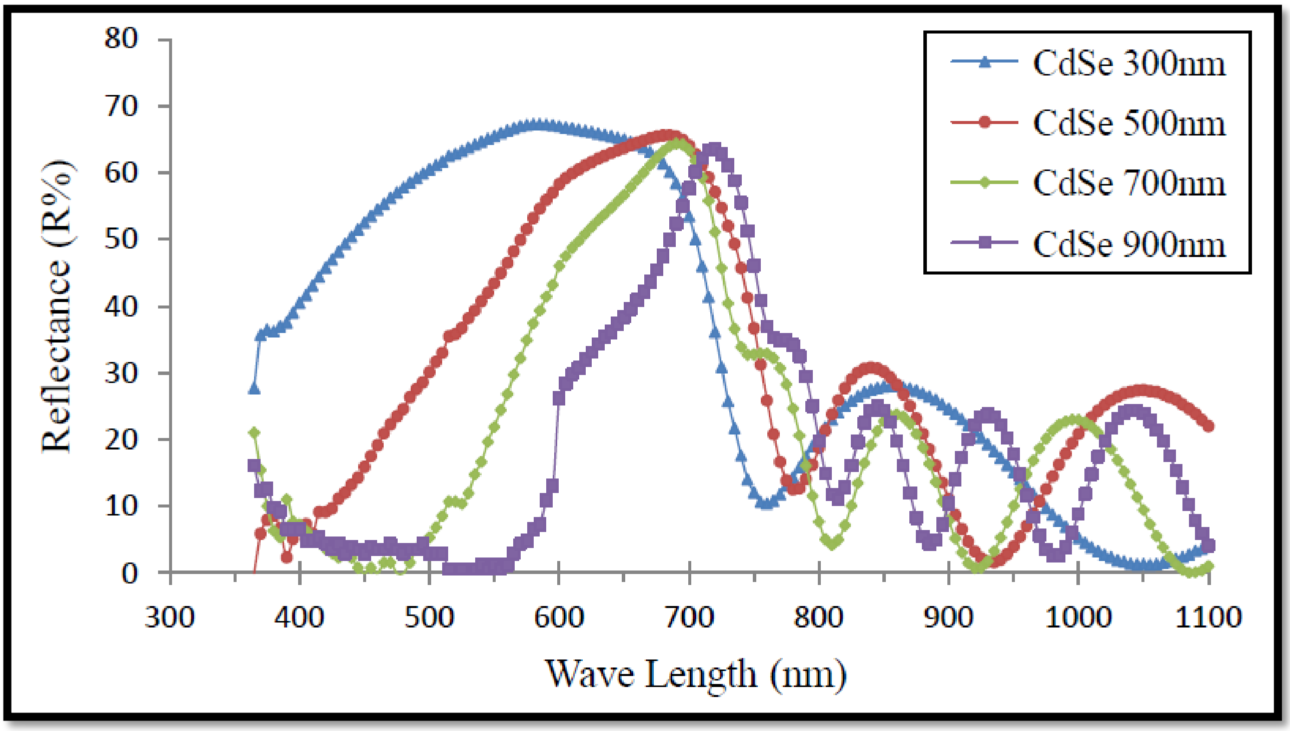

Figure (5) Variations in the % reflectivity spectrum for (CdSe) films made with various thicknesses as a function of wavelength.

Figure(6) depicts the alteration in the absorption coefficient for selenide films as a function of incoming photon energy. cadmium prepared with various thicknesses (300, 500, 700, 900) ±20 nm, as shown in the figure, For the energy ranges located within the Visible region of the electro magnetic Spectrum, it is obvious how the absorption coefficient increases with a direct increase with the energy of the incident photon and for each prepared thickness, in addition to the significant increase in the value of the Absorption coefficient with the increase in the thickness of the film prepared to a value greater than (10^4 .cm^{-1}). This is brought on by an increase in the degree of crystallization as well as the way that the absorbance interacts with the absorption coefficient. The absorbance spectrum and the absorption coefficient are equally related to the thickness of the film and the results that follow (explained above in the absorbance section).

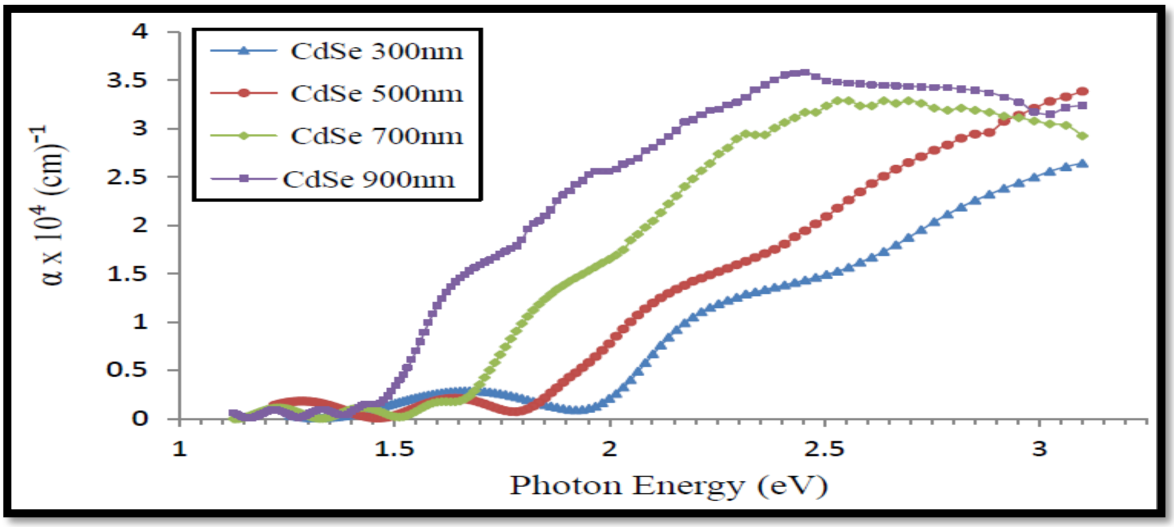

Figure (6) Changes in absorption coefficient for (CdSe) films made with various thicknesses as a function of incoming photon energy.

Conclusion

The structural and optical properties of CdSe thin films prepared by thermal evaporation were systematically studied. XRD results confirmed a polycrystalline hexagonal structure with enhanced crystallinity at higher thicknesses. Optical measurements revealed a direct band gap that decreases with increasing film thickness. The observed optical behavior suggests that CdSe thin films are suitable for optoelectronic applications such as photodetectors and solar cells.

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