Research Article

Influence of Doping on Optical Properties of (CdS:Fe^{+3})Thin Films Prepared by Chemical Spray pyrolysis

Karrar Mahdi Saleh

Ashur Secondary School, Directorate of Education Baghdad Rusafa first, Ministry of Education, IRAQ
*Correspondent Author Email: Amaramar123h@gmail.com

A r t i c l e I n f o	
	Abstract Undoped CdS and doped with iron CdS:Fe^{+3} thin films have been prepared by chemical spray pyrolysis method on The glass different temperatures substrate of cadmium nitrate solution with constant thickness (450 ± 5 nm), and study the effect of the percentage of doping with iron on optical properties of prepared films. The optical properties have been studied from transmittance and absorbance spectral within wavelengths range (380-900 nm). The results showed that all the prepared films have direct electronic transitions and optical energy gap between (2.31-2.44) eV. They also showed that the transmittance and optical energy gap of films prepared from nitrate solution increase with increasing of substrate temperature, then transmittance start downward with The continued increase in temperature (673, 723) k, and a decrease in the optical energy gap with increasing doping percentage with iron.. **Keywords**: : CdS :Fe^{+3}, CSP, Optical properties, doping, iron.

الخلاصة

تم في هذا البحث تحضير اغشية رقيقة من كبريتيد الكادميوم غير المشوبة (CdS) والمشوبة بالحديد (CdS:Fe^{+3}) بطريقة التحلل الكيميائي الحراري (CSP) على قواعد زجاجية وبدرجات حرارة مختلفة من محلول نترات الكادميوم بسمك ثابت (nm 5±430) ودراسة تأثير نسب التشويب بالحديد على الخصائص البصرية للأغشية المحضرة. تم دراسة الخصائص البصرية من خلال دراسة طيفي النفاذية والامتصاصية ضمن الاطوال الموجية (nm 900-380). بينت النتائج ان جميع الاغشية المحضرة تمتلك انتقالات الكترونية مباشرة وبفجوة طاقة بصرية تتراوح بين (eV 2.44-2.31). كما اظهرت نتائج القياسات البصرية للأغشية المحضرة من محلول النترات زيادة في قيمة النفاذية وفجوة الطاقة البصرية مع زيادة درجة حرارة القاعدة , ثم تبدأ النفاذية بالنقصان مع استمرار زيادة درجة الحرارة k (723 ,673), ونقصان في فجوة الطاقة البصرية نتيجة التشويب بالحديد.

Introduction

The term thin films is used to describe a layer or several layers of solid atoms that are deposited on a solid substrate so that the thickness of the thin films is less than (1μm) [1].

Thin-film technology is one of the most important technologies that has contributed to the development and study of semiconductors, which have recently gained considerable interest in nanotechnology researchers and have given a clear idea of many of the physical and chemical properties of these substances whose properties are difficult to obtain naturally [2].

The importance of semi-conductor materials in the scientific and industrial fields has been emphasized for its unique physical characteristics. It is used in many applications such as transistor, integrated circuits, diodes used as emitters, light emitting diodes, solar cells, photovoltaic filters, reagents And magnetic memory devices [3][4].

The optical properties of the (Fe^{+3}) non - deformed and iron-coated (CdS) thin films were studied. The permeability and absorption measurements of all samples were included within the range of wavelengths (380-900) nm, the reflectivity and many optical constants were

calculated by studying the spectral change of permeability and absorption of these thin films such as absorption coefficient, optical Energy gap, coefficient of inertia, refractive index and real and imaginary electrical insulation constant.

Materials and Methodology

Cadmium supplied thin films were introduced in a chemical degradation manner:

The water solution of the cadmium hydrothermal nitrate Cd $(NO_3)_2.4H_2O$ was a quick soluble white substance in water of molecular weight 308.47g / mol and purity 99.999 % which was a source of cadmium ions Cd^{+2} 0.1M by dissolving a certain weight of cadmium nitrate using a magnetic mixer in a certain volume of distilled water according to the following relationship (1) [5].

$$M = \frac{wt}{Mwt} \times \frac{1000}{V} \qquad (1)$$

Where M: Molecular concentration, W_t :The weight required to melt, V: Volume of distilled water, and M_{wt} :Molecular weight of matter.

In the same way, the thiourea solution CH_4N_2S, a white soluble powder 76.11 g/mol with purity 99% and 0.1 mg, is a source of sulfur ions S^{-2}.

Prepare the iron nitrate solution after dissolving a certain weight of iron nitrate in distilled water and (0.1 M) in the same previous way. The iron nitrate solution is added to the cadmium nitrate solution at different volume rates (1, 3, 5) % and at a temperature of 623k.

CdS thin films were prepared from the solution of the cadmium nitrate, and thiourea on the substrate glass at temperature degree 623k, according to the chemical reaction that follows:

$$Cd(NO_3)_2 + CH_4N_2S \longrightarrow CdS + CH_4 + N_2 + 2NO_3$$
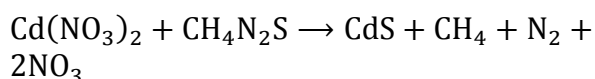
CdS:Fe^{+3} thin films Iron-coated were prepared from the solution of the cadmium nitrate, thiourea and iron nitrate on substrate glass at temperature degree 623k with precipitation ratios (1, 3, 5) % , according to the chemical reaction that follows:

$$Cd(NO_3)_2 + CH_4N_2S + Fe(NO_3)_2 \longrightarrow CdS:Fe^{+3} + CH_4 + N_2 + 5NO_3$$
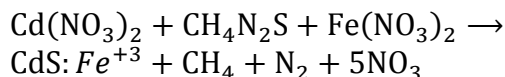
Table (1): shows the volume ratios of iron nitrate solution used in thin films preparation.

CdS (ml)	Fe$(NO_3)_2$ (ml)	Percentage (Fe%)
100	0	0
99	1	1
97	3	3
95	5	5

The solution has an important role in the homogeneity and adhesion thin films and degree of crystallization where the solution of cadmium nitrate was used to prepare CdS thin films, As well as the iron nitrate solution to prepare the doping thin films CdS: Fe^{+3}.

Place the substrate on the center of the electric heater plate to obtain homogeneity in the films and the spray device is vertical on the substrate.

We obtained that the best result was at a height of (29±1) cm. Increasing this distance leads to the volatilization of the solution spray away from the substrata surface. Reducing this distance leads to the concentration of the solution spray in one spot and thus the substrata are not homogeneous.

The spray rate is calculated by the flow of the solution of the solution per minute. The best spraying rate in this experiment is 6 ml / s.

In this study, the solution was sprayed 8s followed by a (2) min and repeated several times until the required thickness was reached.

Air pressure was installed in the glass chamber of the spray device when all thin films were prepared up to $(10^5$ N/m$^2)$ for homogeneous membranes.

Results and Discussion

Figure 1 shows the change in Transmittance (T) with wavelengths for pure and doping with iron thin films (CdS) and the different concentrations. The results show that the permeability increases with the wavelength of all thin films increasing, decreasing with the increase of the doping ratio and increasing at the rate of doping (5%) due to the change in Transmittance and absorption, the change in the energy gap and the formation of localized levels within the energy gap.
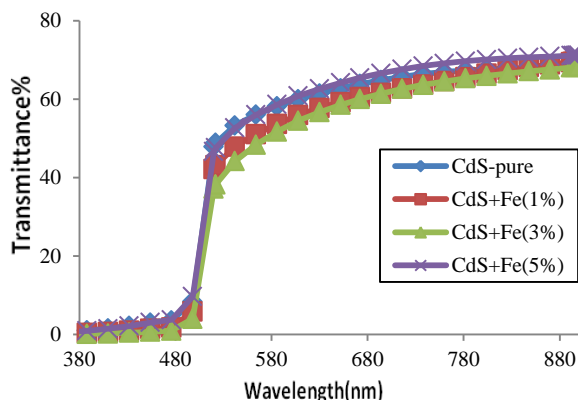
Figure 1: The relationship of a transmittance as a function of the wavelength for the Pure and doping with iron thin films

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Figure 2 shows the change in absorbance (A) as a function of the wavelength of non-porous and iron-coated thin films where we observe that absorption decreases with increasing wavelength of all thin films. This is because the energy of photons falling at high wavelengths (where low energies are insufficient), Figure 2 shows the increase in absorbance with the doping ratios and decreases with the rate of doping (5%). This may be due to the localized levels within the energy gap due to the change in doping ratios, which caused a change in both absorption and transmittance of the thin films.
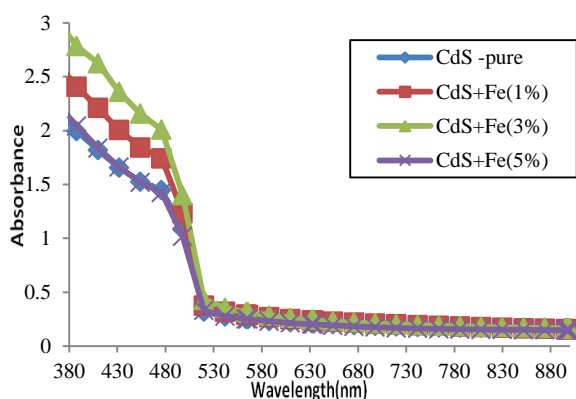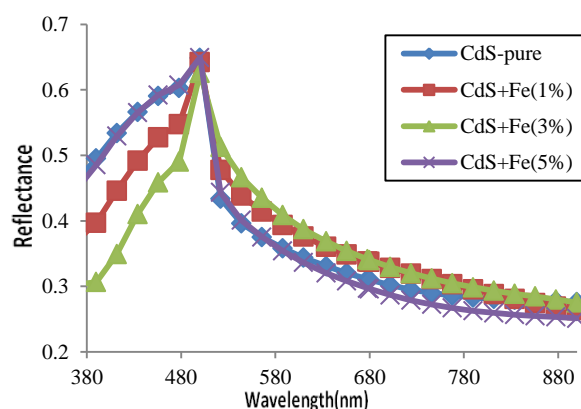

Figure 2: The relationship of absorbance as function of the wavelength for the Pure and doping with iron thin films.

The reflectivity of the surface of the thin films of both pure and doping with iron cadmium sulfide was calculated from the absorption

spectra (A) and Transmittance (T) under the energy conservation law as a function of the projected photon wavelength according equation (2) [6].

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

From Figure 3, which represents the change of reflectivity as a function of the wavelength of the pure and doping with iron (CdS) thin films, we observe that the reflectivity increases with increasing wavelength at the shorter wavelengths (380–480)nm, and then decreases with increasing wavelength at higher wavelengths (480 – 880)nm. And that the reflectivity changes with the increase in the rate of doping because the increase in the rate of doping changes the surface roughness, causing a change in reflectivity.

Figure 3: The relationship of a reflectivity as a function of the wavelength for the Pure and doping with iron thin films.
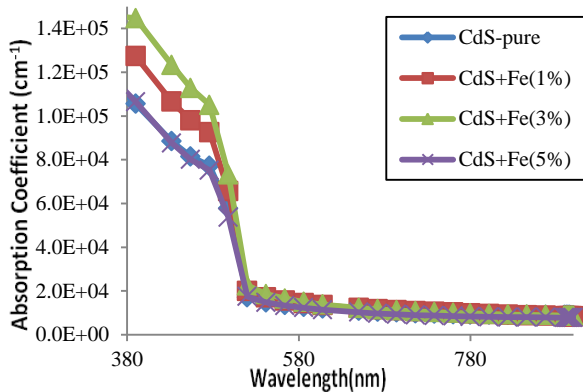
According to the absorption coefficient (α) using the following formula (3) [7].

$$\alpha = 2.303 \frac{A}{t} \qquad (3)$$

Where t : thickness of the thin film.

Figure 4 shows the change in the absorption coefficient as a function of the wavelength of the pure and doping with iron (CdS) thin films. We note that all thin films have a high absorption factor ($\alpha > 104$ Cm^{-1}). This indicates direct electron transitions. The results showed that the increase in the rate of doping resulted in a

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slight increase in the values of the absorption coefficient compared to the before doping condition at the lower energies and then began to decrease slightly at the doping rate (5%). Also, the absorption limits creep slightly with increasing doping. The formation (generation) of local levels within the energy gap in turn led to a mutation the photons with energies of low - lying and then change in the absorption coefficient values.
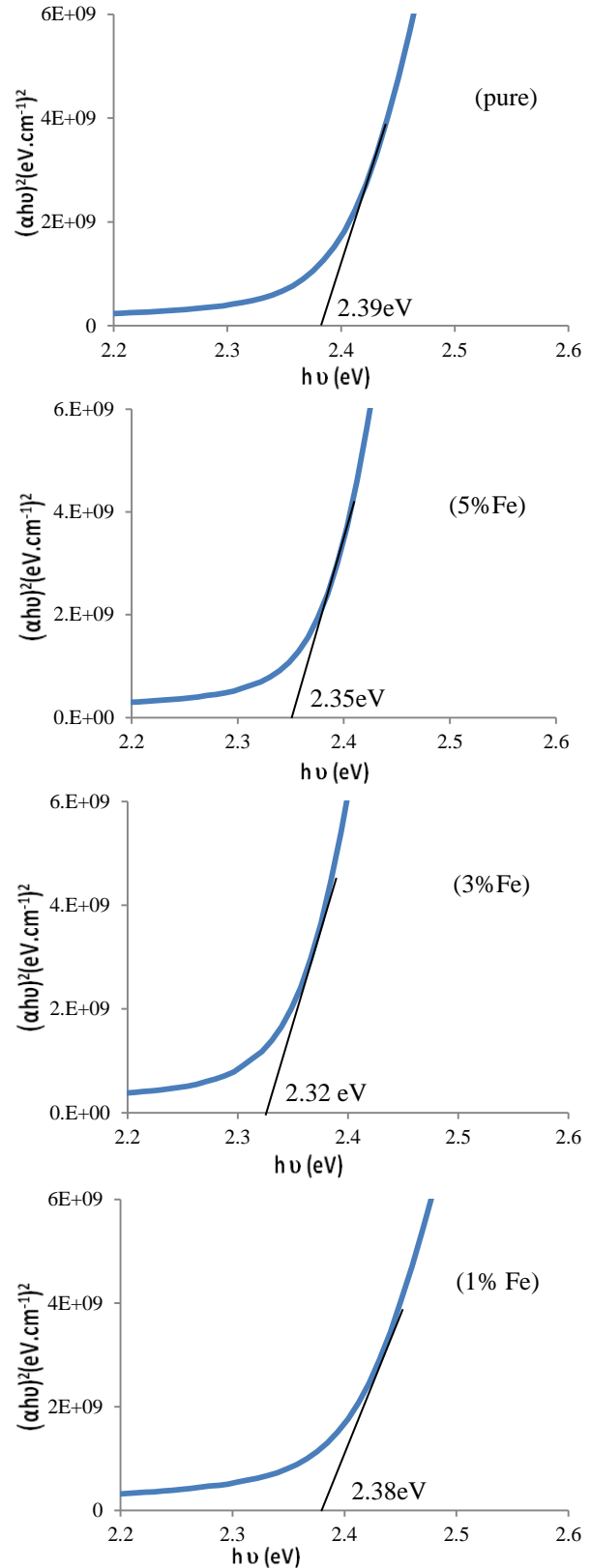

Figure 4: The relationship of the absorption coefficient as a function of the wavelength for the Pure and doping with iron thin films.

The optical Energy gap $\left(E_g^{opt}\right)$ was calculated using the following relationship (4) [8].

$$\alpha h v = B\left(h v - E_g^{opt}\right)r \qquad (4)$$

Where B represents the proportionality constant depends on the nature of the material and r: is the order of the optical transition, depends on the nature of the electron transmission.

And by drawing a graphic relationship between (hυ) and $(\alpha h v)^2$ as in Figure 5. The energy gap is calculated when ($\alpha h v^2 = 0$) is from the intersection area of the tangent with the (hυ) axis, so the intersection point represents the energy gap and we note that The values of the optical energy gap $\left(E_g^{opt}\right)$ decrease with the increase in the rate of doping because of the formation of the local levels within the energy gap and then increase slightly at the ration of (5%), as in Figure 6.

Figure 5: Relationship $(\alpha h v)^2$ with photon energy for the Pure and doping with iron thin films at different rates.

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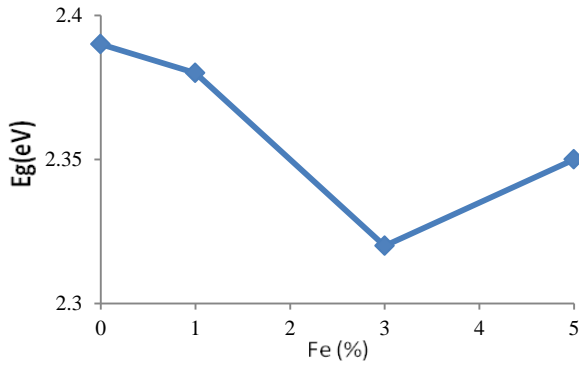
Figure 6: Relationship of the Energy gap with the doping ratios.

The Extinction coefficient (k_o) was calculated according to the following equation (5) [9].

$$K_o = \frac{\alpha\lambda}{4\pi} \qquad (5)$$

Where λ: Wavelength of the electromagnetic spectrum radiation.

Figure 7 shows the change in the Extinction coefficient as a function of the wavelength for Pure and doping with iron (CdS) thin films. Note that the Extinction coefficient decreases by increasing the wavelength, and a sharp decrease at wavelength ($\lambda > 500$ nm) as in Figure (7), due to the decrease in absorbance at high wavelengths. When the falling photon energy is less than the energy gap value, the results showed that the increase in doping rates led to a change in the values of the Extinction coefficient compared with its value before doping. The reason for this change was due to the local levels within the energy gap that led to increasing the absorption coefficient and then changing the Extinction coefficient.

The refractive index (n_o) was calculated using the following relationship (6) [10].

$$n_o = \left[\left(\frac{1+R}{1-R} \right) 2 - (K_o 2 + 1) \right]^{1/2} + \frac{1+R}{1-R} \qquad (6)$$

Note from Figure 8, which represents the change of refractive index as a function of the wavelength of the milled and undamaged membranes and that the refractive index increases with wavelength increase when

($\lambda<500$nm). Then starts with decreases when ($\lambda>500$nm) and that the refractive index changes with increasing deflection.
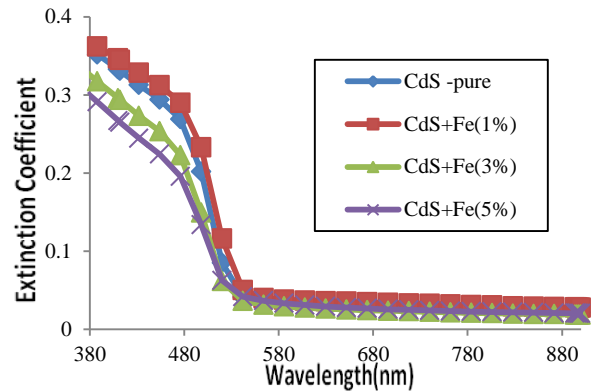
Figure 7: The relationship of Extinction coefficient as a function of the wavelength for the Pure and doping with iron thin films.

It is also noted that the nature of the refractive index curve is similar to the nature of the reflectivity curve and that the highest value of the refractive index curve corresponds to the energy gap, indicating that direct electronic transitions occur in that range of energy.
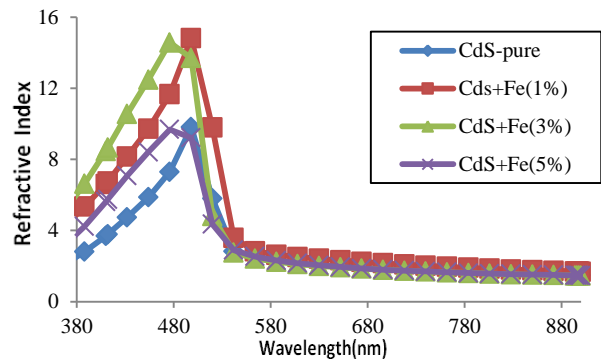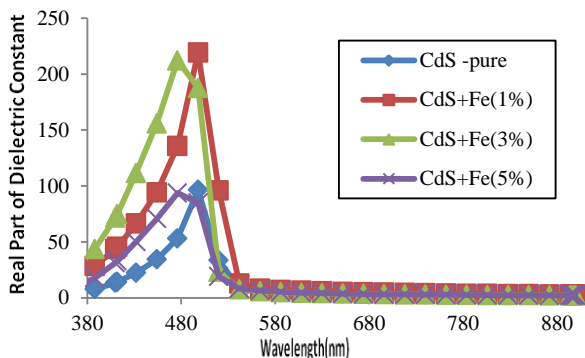

Figure 8: The relationship of the refractive index as a function of the wavelength for the Pure and doping with iron thin films.

The Dielectric constant was calculated by its real (ε_r) and imaginary (ε_i) parts according to the two equations (7) (8) [11].

$$\varepsilon_r = n_o^2 - k_o^2$$
$$\varepsilon_i = 2n_o k_o \qquad (7)$$

Note that the values of (ε_r) and (ε_i) increase with wavelength increase up to ($\lambda \approx 500$ nm) and then start with decreases and for all thin

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films. Also note that the values of the dielectric constant in its parts change with increasing doping ratio and that the real part values are greater, than the imaginary part values as in figure 9 and 10 representing the change of the real and imaginary dielectric constant respectively as a function of the wavelength.

Figure 9: The relationship of real part of dielectric constant as a function of the wavelength for the Pure and doping with iron thin films.
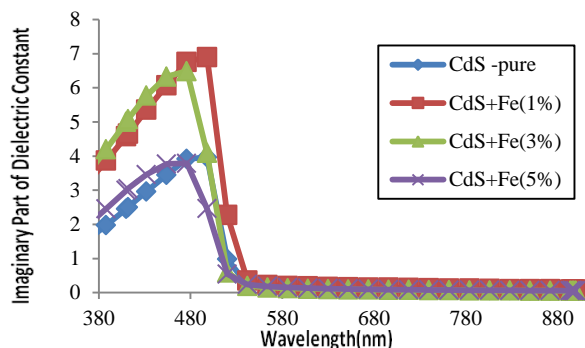
Figure 10: The relationship of imaginary part of Dielectric Constant as a function of the wavelength for the Pure and doping with iron thin films.

Conclusions

Iron replaces in lower concentrations and becomes interstitial with increased concentration in the nitrate-forming thin films and the optical energy gap of the pure CdS is greater than the optical energy gap of the Thin films CdS: Fe^{+3} and the energy gap decreases with the increase of the doping rate and

The change in the doping of the thin films in iron led to a change in the values of the extinction coefficient, refractive index and dielectric constant in real and imaginary parts within wavelengths (380 - 520) nm.

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