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STUDYING THE EFFECT OF AG DOPING ON THE STRUCTURAL AND OPTICAL PROPERTIES OF CDO THIN FILMS PREPARED BY CHEMICAL SPRAY PYROLYSIS METHOD

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Abstract

In this work, thin films of undoped and Ag-doped CdO with (1and 3) wt.% were prepared by using spray pyrolysis method on glass substrate at of 350ºC with films thicknesses of (160-190) nm using spraying rate and pyrolysis time is 5 ml/min an 5sec respectively. The X-ray diffraction investigated the structural types of the CdO thin films after and before doped by Ag, XRD analysis showed that CdO:Ag films are highly polycrystalline and exhibit cubic crystal structure with (111) preferred orientation. However, the peak for all CdO:Ag films became more intense with a slight variation. The optical properties measure by ultra violet spectra, the optical study shows the spectral transmission and the optical energy band gap increases from 64.77% and 2.50 eV to 71.11% and 2.70 eV respectively depending upon the Ag content in the films, in contrary with the absorbance that increases with the decrease in wavelength and decreases with the increasing Ag doping concentration.

Keywords: Cadmium Oxide, Spray Pyrolysis, XRD, Thin film, Ag doped CdOCell.

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1. Introduction

Cadmium oxide (CdO) has high electrical conductivity and high optical transmittance with a moderate refractive index in the visible region of the solar spectrum [1]. Because of their low resistivity and high optical transmittance, Cd0 thin films have been used as Transparent Conducting Oxide thin films. Its optical band gab is about 2.16 eV at room temperature depending on the kinds of techniques that are used and the preparation conditions of the method used [2]. The combination of high transparency on the visible ranges of the electromagnetic spectrum, high electrical conductivity, and high carrier concentration; these properties make CdO thin films very useful for many applications like solar cells , phototransistor, diodes , gas sensors , heat mirrors, antireflection coatings , transparent electrodes, photodiodes, etc [3]

The commonly used methods of preparation of semiconductor thin films are spray pyrolysis, sputtering, sol gel, vacuum evaporation , PLD, chemical bath deposition technique (CBDT), etc.[4].The optoelectronic semiconductor material cadmium oxide has been extensively studied as epitaxial and polycrystalline thin films prepared by different techniques because of its unique optoelectronic and other properties with the hope of exploring potentialities for fabrication of new scientific and technological devices.[5]

Many researchers prepared polycrystalline CdO thin films and studied their structural, optical, and electrical measurements. Oday Ali Chichan prepared CdO thin films by sol-gel technique with spin coating method on glass substrates, and doped with Ag with a relatively high concentration of Ag (2.5%, 5%, 10%, and 15%) in order to obtain changes in structural and electrical properties of Ag; CdO doped thin films, in 2.5%CdO:Ag grain size D increase and this means that crystallization increasing is due to the particle size increased, for 5%CdO:Ag, 10%CdO:Ag and 15%CdO:Ag[6].

Jinan Ali Abd prepared CdO and In doped CdO with (2,4,6, and 8%) ratio thin films by spray pyrolysis method on glass substrate at a temperature of 350ºC with film thicknesses of (225-254 nm). The X-ray diffraction patterns confirmed that the In-doped and un-doped CdO films of polycrystalline cubic crystal structure with no evidence of In_2O_3 and CdO or mixed phases. Optical transmission of all films increased while increasing in wavelength, and it's increased as In-doping level increased. The optical band-gap is slightly increases with the increasing In doping due to Burstein-Moss effect [7]. The aim of this work is to prepare CdO thin film by chemical spray pyrolysis and study the effect of Ag doping with relatively concentration Ag (1%, and 3%) in the structural and optical characteristic of CdO Thin film.

2. Experimental Part

2.1 Preparation of Thin Films

Transparent and conducting CdO thin film was deposited on glasses substrate by used Spray Pyrolysis Method. The CdO thin films prepared from using the powder of cadmium acetate $Cd(CH_3COO)_2.2H_2O$ with white color and 1.332 gm/mol .In 0.1M, 1.332gm of the acetate diluted with 50 ml distilled water. Solution used to prepare Ag:CdO thin films in this study , the indium was used as a dopant element. Its solution was prepared from dissolved 2.21 gm of Ag (221.177 g/mol) in 50 ml of distiller water at 0.1M. The result solution was added to the same solution of CdO which prepared above to dope it in a ratio of (1% and 3 %). To ensure a perfect solubility of the solution mixture, a magnetic stirrer was used. Microscope glass substrates, after subject to the cleaned process, were place on hot plates fixed at 350 ºC. optimized depositions parameter was used, such as spray time 5s ,substrate spray nozzle distance (29 cm), spray interval (55 s) and carrier gas pressure (compressed air 10^5 N.m-2).

2.2 The Thickness Measurement

The Film thickness (t) was measured using the optical interferometer method; this way was based on interferences of light beams reflect from thin films surface and substrates bottom. He-Ne Laser of wavelength (632.8 nm) it use and the thickness is determine using this formula

Where X is fringes width, Δx is that shifted distance between two fringes and λ is wavelength of laser lig

2.

$$t = \frac{\Delta X}{X} \cdot \frac{\lambda}{2} \quad \ldots\ldots (1)$$

2.

X-Ray Diffraction measurement was recorded and compared with the JCPDS-International Center for Diffraction Data cards, (using Philips PW 1840) XRD meter systems that record the intensities as a functions of Bragg's angles. The sources of radiations its Cu(kα) with wavelength λ=1.5406Å, current 30 mA and voltage 40kV. The Scanning angle 2θ is vary on the range of (10–80) degree.

The crystallite size all peak was calculated using Scherrer's formula [8].

$$D = \frac{k\lambda}{\beta \cos\theta} \quad \ldots\ldots (2)$$

where k is the shpe factor , β is the Full Width at Half Maximum must be in radians and θ correspond to diffraction angle.

2.3.2 Optical Measurement

A double–beamUV-VIS-NIR210A spectrophotometer (VRIAN, made in Australia) was used to determine the transmittances and absorptions of CdO films after and before doping to Ag transmittance, absorbance data can be used to calculated the Absorption coefficient of the film at different wave lengths, which has been used to determine the band gap (Eg) by the following equation:[9]

$$\alpha h\nu = A\left(h\nu - E_g\right)^{1/2} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where A is constant inversly propertion with the amorphosity , α is the absorption coefficient and $h\nu$ is the incidents photon energy.

3. Results and Discussions

3.1 X-Ray Diffractions Measurement

The effect of Ag doping with relative concentration Ag (1%, and 3%) on the CdO films structure has been studied. The (XRD) pattern of the Ag doped CdO thin films prepared by spray pyrolysis technique at glass substrate temperature 350 °C is illustrated in Figure (1),XRD for all the patterns show a polycrystalline with cubic structure and also it can be clearly seen that all films are preferentially orientated along (111) crystallographic directions corresponding to 2θ=10 to 80, as well as the emergence of four diffraction peaks { (200) , (202) , (311) ,(222) }also is seen from this figure that the intensity of the peaks decrease with increasing of Ag concentration.

The structural parameters such as diffraction angle (2θ), lattice spacing (d), , full width at half maximum (FWHM), and the phases identified along with (hkl) planes were evaluated from these spectra and presented in table (1) .It is important to mention that when increase the Ag concentration the crystal size (C.S) deceases and the full width at half maximum increasing, (C.S) is calculated from the full width at half maximum (FWHM) β of the preferential orientation diffraction peak by using Scherrer equation, eq. (2) as shown in table (1). The results we obtained is similar to the results of the paper[6] .

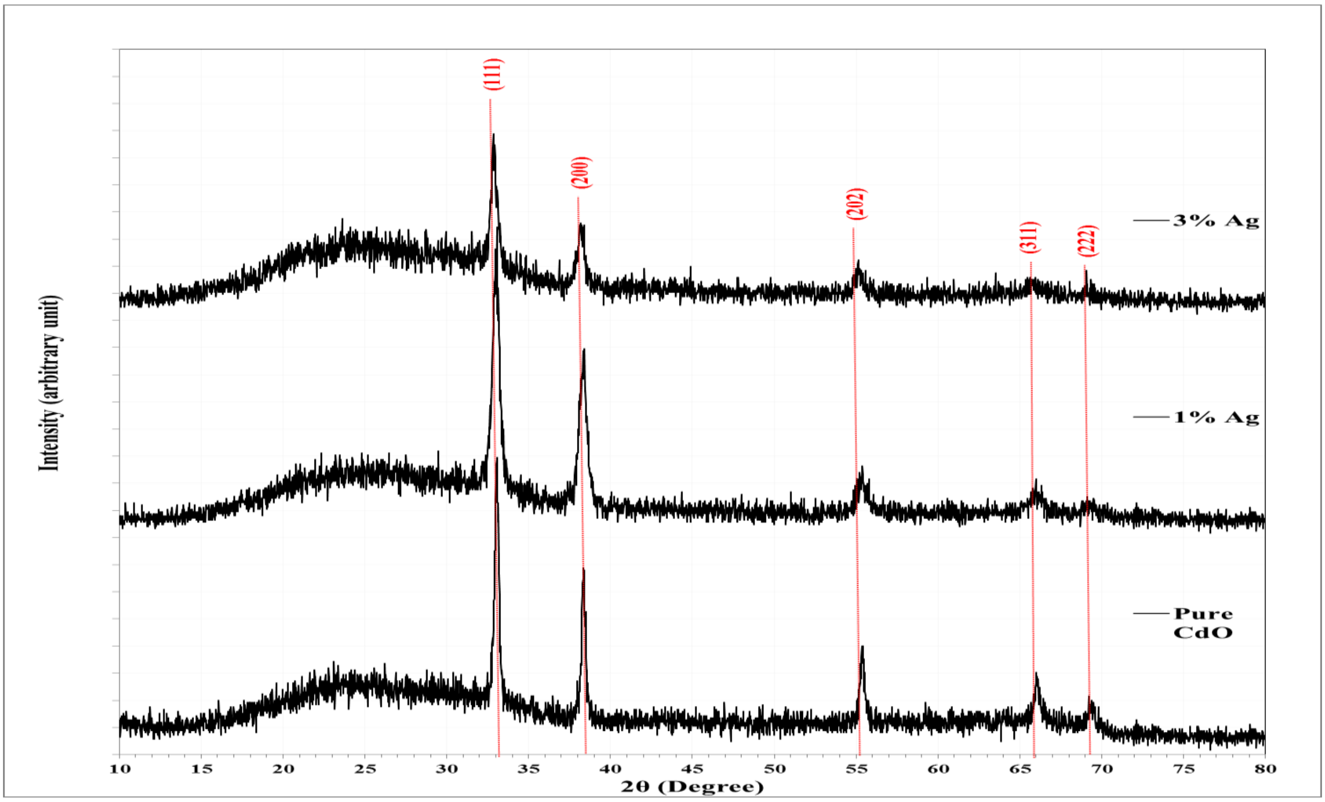

Fig (1): The X-ray diffraction patterns of the prepared un-doped and doped CdO films with Ag particles

Table (1): X-ray diffraction parameters of the prepared un-doped and doped CdO films with Ag particles: the diffraction angle 2θ, interplaner distance (d) , FWHM and crystal size C.S

sample	2θ (Deg.)	FWHM (Deg.)	dhkl Exp.(Å)	C.S (nm)	dhkl Std.(Å)	hkl	card No.
Pure	33.0799	0.2800	2.7058	29.6	2.7130	(111)	96-101-1004
	38.3476	0.3190	2.3454	26.4	2.3495	(200)	96-101-1004
	55.3995	0.3620	1.6571	24.8	1.6613	(202)	96-101-1004
	65.9891	0.3960	1.4145	23.9	1.4168	(311)	96-101-1004
	69.4104	0.4150	1.3529	23.3	1.6613	(222)	96-101-1004
1%Ag:CdO	33.0391	0.3700	2.7091	22.4	2.7130	(111)	96-101-1004
	38.3796	0.4730	2.3435	17.8	2.3495	(200)	96-101-1004
	55.3720	0.5140	1.6579	17.5	1.6613	(202)	96-101-1004
	65.9647	0.5360	1.4150	17.7	1.4168	(311)	96-101-1004
	69.0984	0.6208	1.3583	15.5	1.6613	(222)	96-101-1004
3%Ag:CdO	32.8184	0.4100	2.7268	20.2	2.7130	(111)	96-101-1004
	38.1589	0.4800	2.3565	17.5	2.3495	(200)	96-101-1004
	55.1513	0.5900	1.6640	15.2	1.6613	(202)	96-101-1004
	65.6116	0.6010	1.4218	15.7	1.4168	(311)	96-101-1004
	69.0542	0.6820	1.3590	14.1	1.6613	(222)	96-101-1004

Both the crystallite size and lattice strain contribute to x-ray broadening as Cauchy-like profile, so the breadth (β_{hkl}) is just the sum of the two broadening due to these effects using Debye-Scherrer's formula and lattice strain broadening (ε) [10]

$$\beta_{hkl} = \frac{k\lambda}{\beta\ cos\theta} + 4\ \varepsilon\ tan\theta \qquad ....(4)$$

$$\beta_{hkl} cos\theta = \frac{k\lambda}{L} + 4\ \varepsilon\ sin\theta \qquad ....(5)$$

From the linear fit of the plot between $\beta_{hkl} cos\theta$ against 4sinθ, the crystalline size was determined from the y-intercept, and the slope represent the strain ε as shown in Figure (2).

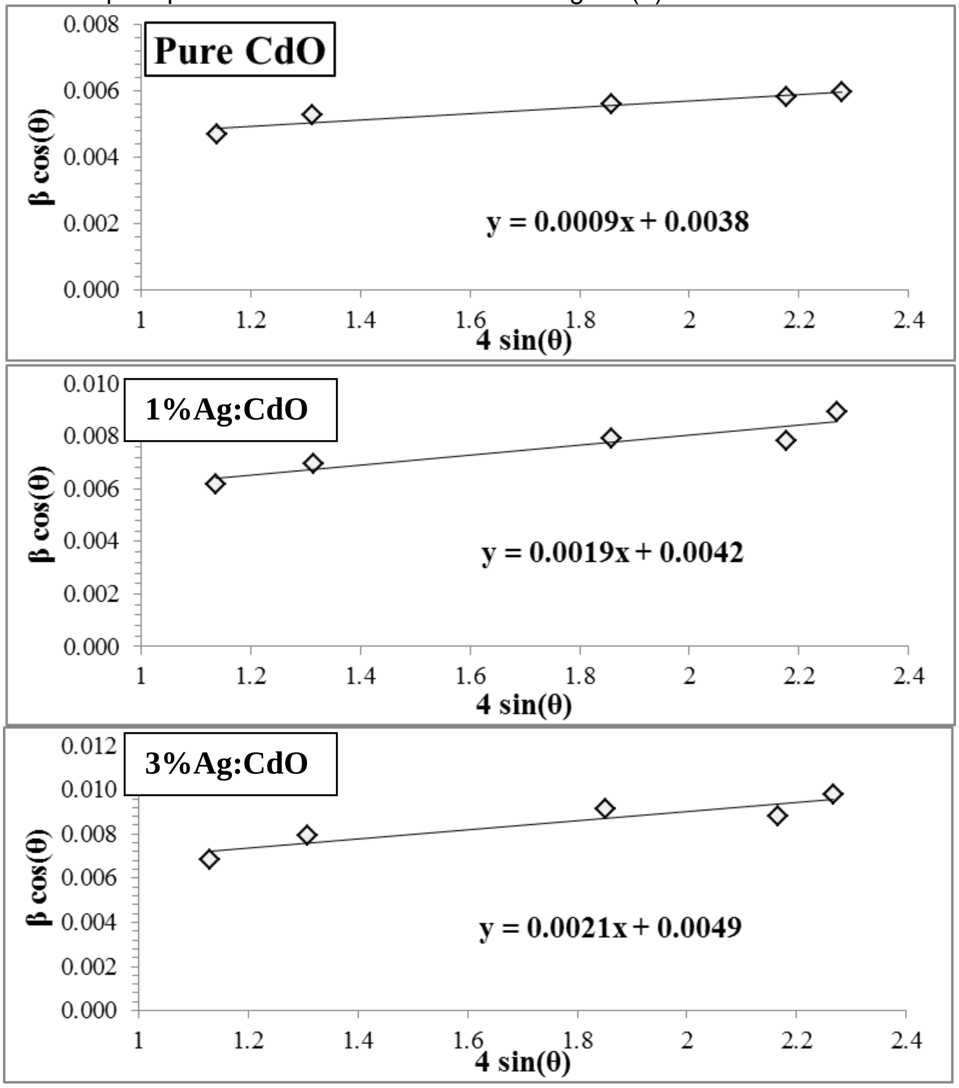

Fig (2): Williamson and Hall plot of for un-doped and doped CdO films with Ag particles

The non-uniform strain and domain crystalline size for pure and Ag doped samples where shown in Table (2). It is appears that the crystalline size values decrease from (36.5 nm) for CdO thin film to (28.4 nm) at 3% Ag atomic ratio. While, the strain in lattice has apposite behavior with maximum value of where the main effective on strain in lattice reduce its crystalline size.

Table (2): Domain crystalline size and non-uniform strain for un-doped and doped CdO films with Ag particles

Sample	Non uniform strain	domain size (nm)
Pure CdO	0.0011	36.5
1% Ag:CdO	0.0023	32.8
3% Ag:CdO	0.0029	28.4

3-2. Optical Properties

Optical properties have a great importance in the study the behavior of optical semiconductor materials, it is useful in the task of determining the nature of the practical application that can be used to record film

material [12].These properties were important for the understand of the mechanisms of electrons transitions between energy band during the measuring of absorption and transmissions of a semiconductors. [13]
Theoptical transmittance spectra forum-doped and Ag doped CdO films were measured in the range from (300–1100) nm at room temperature on air as seen in the fig (3) it was clearly noted that the transmissions of all films increasing as Ag doping level increases, These spectra show that adding Ag to CdO improves the transmittance for all the deposited samples. The un-doped films show a transmittance of 64.77% (800 nm) and the doping increases the transmittance value up to 71.11% (800 nm) for the 1 wt.% Ag doping. This effect of Ag doping on the transmission of CdO films may be due to the structural and surface effects. These effects such as better crystallinity, less surface irregularity and defect density can increase the transmission.

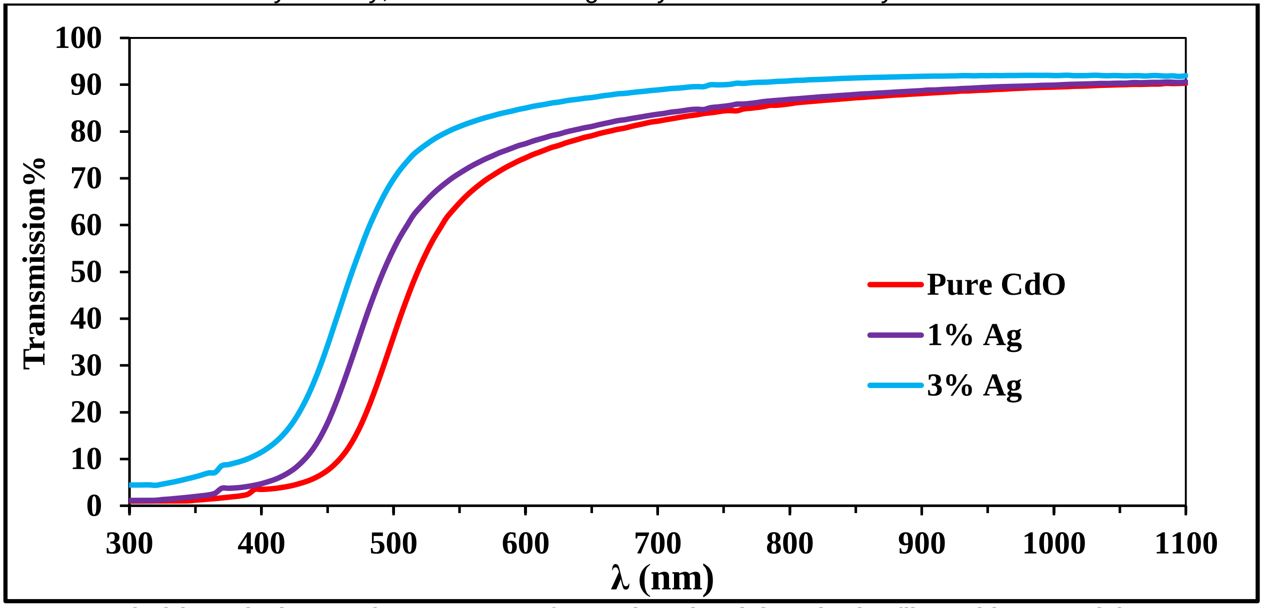

Fig (3) :Optical transmittance spectra for un-doped and doped CdO films with Ag particles

The ability of a material to absorb light is measured by its absorption coefficient, equation (3). The variation of the optical absorption coefficient with wavelength is shown in Figure (4). It was clearly seen that the absorbance increases with the decrease in wavelength and decreases with the increasing Ag doping concentration

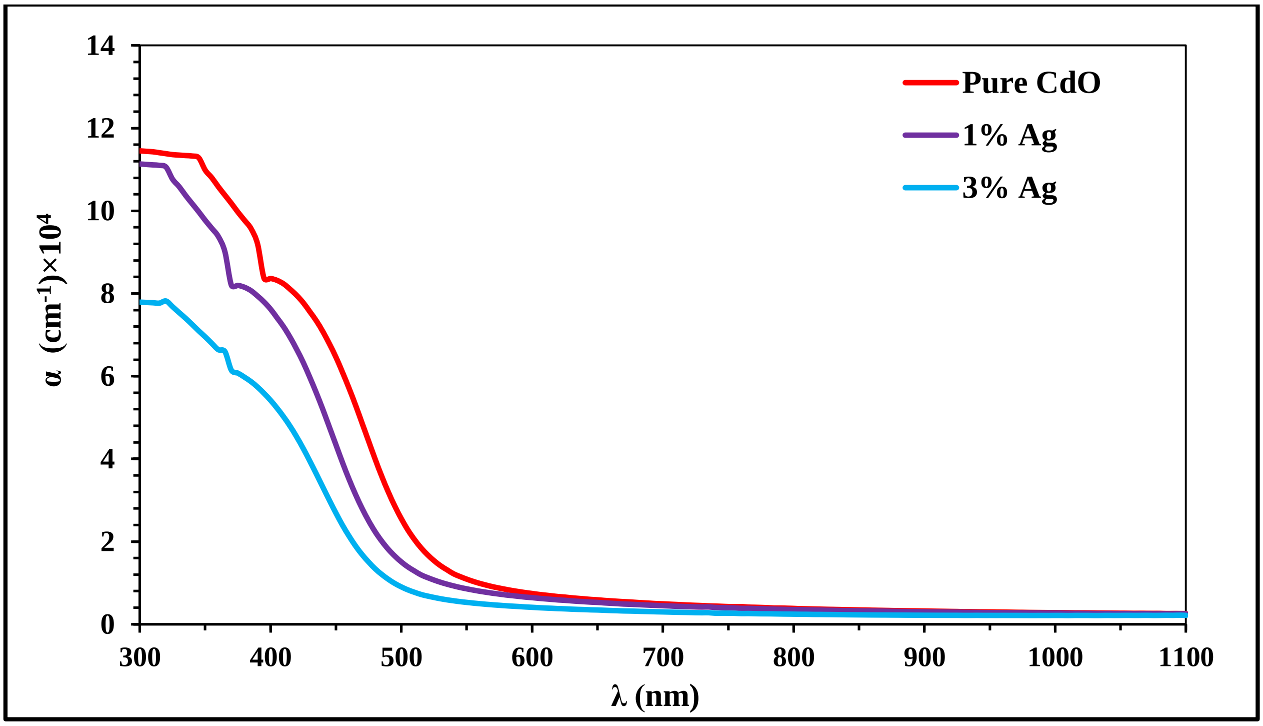

Fig (4): The variation of the absorption coefficient for un-doped and doped CdO films with Ag particles

The optical energy gap values (Eg) for CdO and CdO:Ag thin films have been determined, The E_g was predestined by presume a direct transition between valance and conduction bands and its values obtained by extrapolating the linear portion of the plots of $(\alpha h\nu)^2$ versus (hν) to α= 0. These plots are given in Figure (5). The optical band gap of the films slightly increases with the increasing Ag doping. For CdO film E_g equals to 2.50(eV) and the E_g values of Ag (1 and 3%) doped CdO films equal to 2.60 and 2.70(eV) respectively. This slight shift of the band gap with the increase in Ag doping is mainly related to the increase of carrier density [14,15].

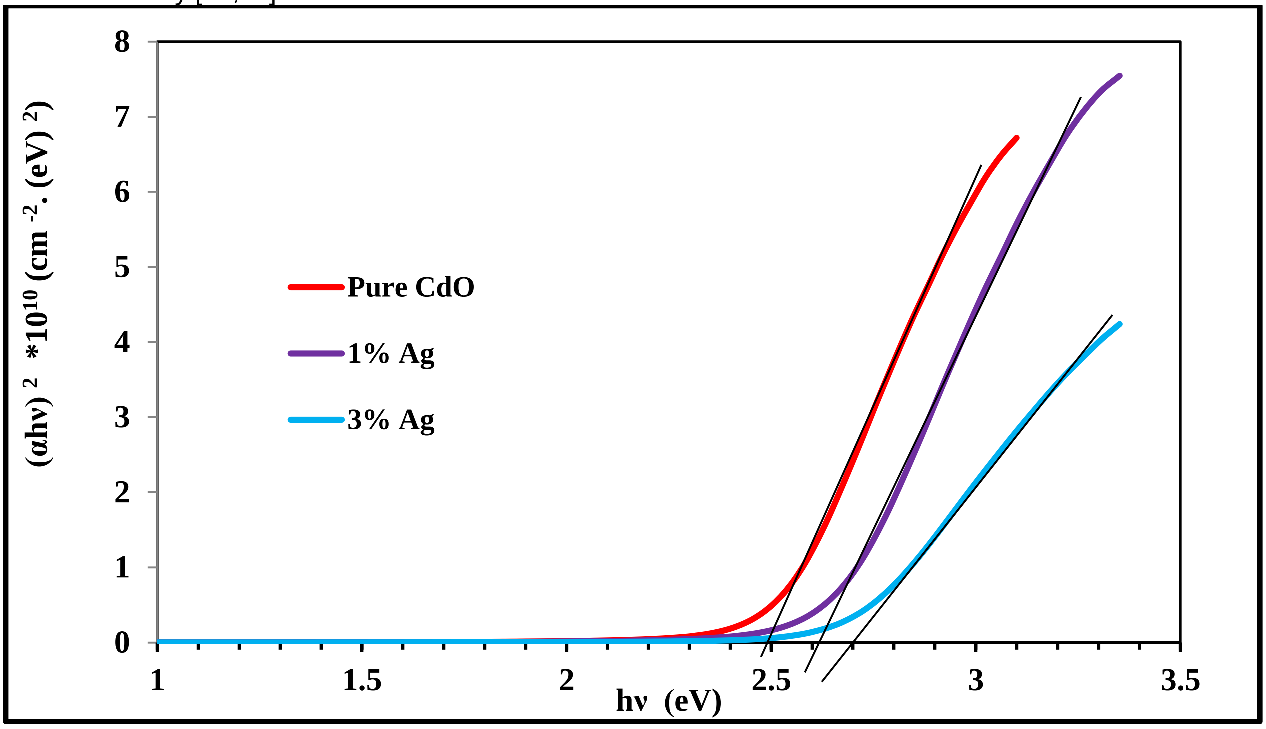

Fig (5): the (αhv)2 versus photons energies (hv) for un-doped and doped CdO films with Ag particles

The refractive index is the ratio between the speed of light in vacuum to its speed in material which doesn't absorb this light. Figure (6) shows the variations of the refractive index as a functions of the wavelength for un doped CdO and Ag doped CdO thin films. It indicates that the refractive index decreasing with increasing the increasing Ag doping.

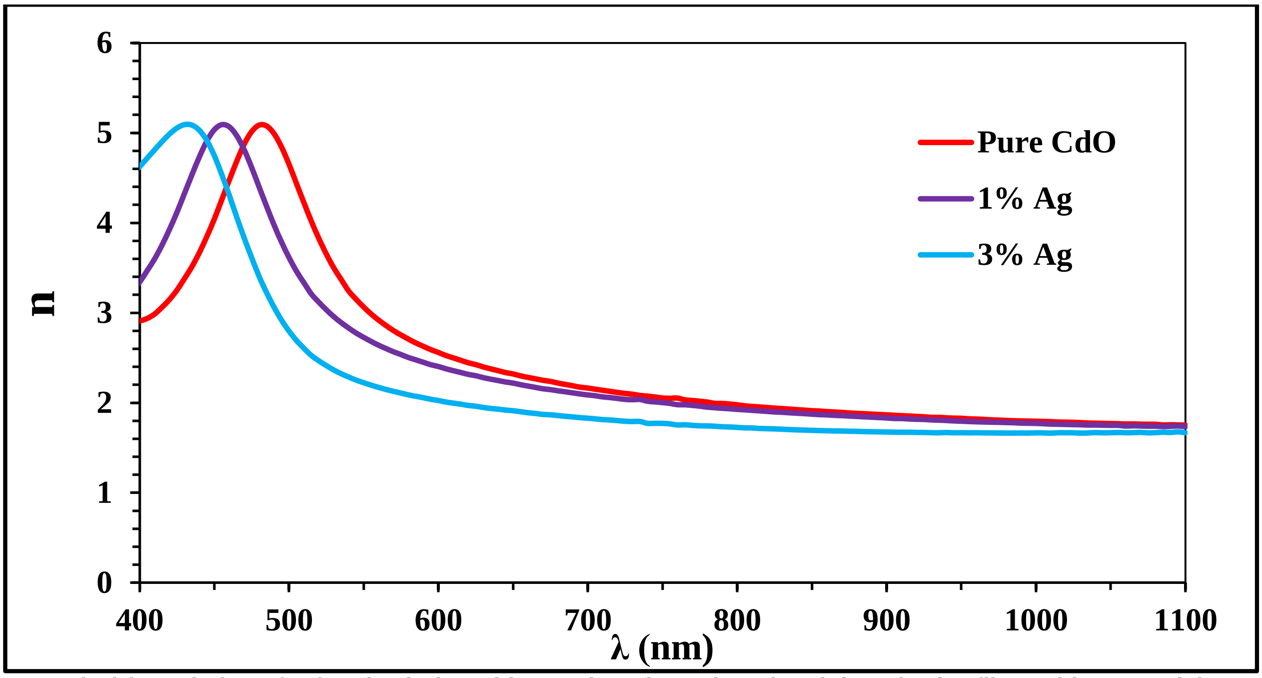

Fig (6): Variation of refractive index with wavelength un-doped and doped CdO films with Ag particles

4-Conclusion

Cadmium Oxide thin film was deposited by Spray Pyrolysis Technique at a substrates temperatures 0f 350 ºC. The thickness of the films are about 180-190 nm were calculated by Gravimetric method and interference fringe .CdO thin films were doped with relative concentration Ag (1%, and 3%).XRD patterns show that all films are polycrystalline of cubic structure and preferentially orientated along (111) crystallographic directions and by Ag doping the preferential orientation peak became sharper and more intense, it is important to mention that when there is an increase of the Ag concentration the grain size (D) decreases and the full width at half maximum increases.

The optical properties measure by (UV-VIS) shows the transmissions of un-doped films is64.77% (800 nm) and the doping increases the transmittance value up to 71.11% (800 nm) for the 1 wt.% Ag doping. It was noted from the study that the absorbance increases with the decrease in wavelength and decreases with the increasing Ag doping concentration. As can be seen clearly that the optical band gap of CdO thin films become wider with increasing Ag doping as well as the refractive index decreasing with increasing the Ag doping.

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