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The Effect of Non-Thermal Plasma of the Structural and Optical Properties of cadmium Oxid (CdO) Thin Films Prepared by Chemical Spray Pyrolysis

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Abstract: ***This work, cadmiuum Oxide Thin film was deposite by chemical Spray Pyrolysis method on the glasses substrates on 350 Ċ with thickness about (185) µm was calculated by interference fringe and exposure to non-thermal plasma period between (5-10-15) min respectively, Plasma has been called the fourth state of matter, the other three being solid , liquid , and gas , its defined as a collective of mobile positively and negatively charged particles and natural atoms, the non thermal plasma is one of the types ofit, In this type the electron temperature is much larger than the temperature of the remains plasma components In other words, ($T_e >> T_i \approx T_n$) . theX-Ray Diffraction investigated the Structural types in the CdO Thin film after and before exposure to unbalanced plasma , it showed that the intense of the peaks decreased with increasing time exposure to cold plasma as well as appearance of another new peaks in the diffraction pattern for CdO film. The Surfaces Morphology and Roughness of the samples was studied by Atomic Force Microscopy , the Average Roughness and Root Mean Square roughness surface of CdO thin film decrease with increasing the exposure time of non –thermal plasma . The optical properties measure by ultra violet spectra (UV-VIS), the optical study shows the band energy gap decreasing with exposing time to cold plasma which ranging between (2.6- 2.2) eV , The average Optical Transmittance of CdO film on the ranged 340–1100 nm, is about 80%. To 55% .***

Keywords: cadmiumm Oxide , spray pyrolysis method, AFM , XRD , Thin film , non thermal plasma

1. Introduction

Cadmiumoxide(CdO) has highelectricalconductivity and high optical transmittance with a moderate refractive index in the visible region of the solar spectrum {1}. Cd0 thin films have been using as Transparent Conducting Oxide thin film due to that low resistivity and high optical transmittance , its optical band gab is about 2.16eV at room temperature depend on the kinds of techniques that use and the preparation conditions of the method use{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 application like Solar cells , phototransistor , diodes , gas sensors , heat mirror , antireflection coatings , transparent electrodes, photodiodes, etc{3}

In recent years it has found various techniques used to prepared CdO thin films such as thermal evaporation in vacuum deposition , sputtering techniques, chemical vapor deposition , pulse laser deposition , thermal pyrolysis deposition , 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 a hope of exploring potentialities for fabrication of new scientific and technological devices.{6}

Many searchers prepared polycrystalline CdO in thin film forms and studied their structural, Electrical and Optical measurements .Dou et al in studythat influenced of n-Type doped CdO with In or Y. hve been investigate by highly-resolutions Ultraviolet and -XRay photoemissions spectro scopy. Its found the core level and Valence band feature suffers a shift to highly binding energies due to doping. However that shift is lower than that changed in the width of the occupy Conduction band. this provide a direct measurements of band Gap shrinkages as a results of doping on an Oxide Semiconductor{4}.Guillermostudied the structural and Optical Properties of (ZnO)x(CdO)1-x Thin film obtained by Spray Pyrolysis annealed in air at 450º C. a mixing phase Correspond to Cubic-CdO and hexagonal- ZnO. the changes in the Transmission spectra and in the correspond value of the band- Gap energies was correlate with the intermixing of transparents ZnO crystallite in-between CdO crystallity.{5}

Dr.Jinan Ali Abd prepared CdO and In doped CdO with(2,4,6,and 8%) ratio thin films by spray pyrolysis method on glassy substrate at temperature of 350ºC with films thicknesses of (225-254 nm) The X-ray diffraction confirmed that the In-doped and undoped CdO films of polycrystalline and cubic crystal structure with no evidence of In_2O_3 and CdO_2 or mixed phases . Optical transmission of all film increased while increasing in wave length and that light transmissions of CdO film increased as In doping levels increased the Optical band-

Gap the films slightly increases with the increasing In doping due to Burstein-Moss effect{7}

The aim of this work is prepared CdO thin film by chemical spray pyrolysis and studied the effect of non –thermal plasma in that structural and Optical characteristic of CdO Thin film.

2. Experimental Part

2.1 Preparation of Thin Films

Transparent and conducting CdO Thin film was deposit on glasses substrate by used Spray Pyrolysismethod. Cadmium Acetate (Cd(CH3COO)2·2H2O) was use as a Source materials of Cd it concentrations about 0.1 M was dissolving in 50 Mal re -Distilled Water , The microscope glasses substrates after subject to the cleaned process was place on hot plates until that reach 350Ċ . Optimized depositions parameter such as Spray time (5 S) ,substrate spray nozzle distance (29 cm) , spray interval (55 s) and carrier gas pressure (compressed air 10^5 NM^{-2})

2.2 The Thickness Measurement

The Film thickness (t) was measure used the Optical Interferometer Method; this way was base 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 [8].

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

Where X is fringes width, Δx is that distance between two fringe and λ is wavelength of laser light.

2.3 Film Characterization

2.3.1 Dielectic Barrier Discharge

The samples exposures to non –thermal plasmaperiod between (5-15) min and this cold plasma Produced byDielectic Barrier Discharge(DBD), the DBDConsidered Kind of AC discharge In this type of discharge produced Thermally unbalanced plasma at atmospheric pressure and medium gas temperature{15}.It has been linked voltages generator that work with range (0-3000) Volt with electronic converter (Nova Lite) .the voltage use in this study was (10.2kV).

The electrical transferred was linked to non-thermal plasma device that contains from two poles: Anode (positive electrode), which represents the top side and Cathode (negative electrode), which represents the bottom. Distance separates the poles can be controlled by controlling the rise and descent of the cathode. Glass disc of (2mm) thickness was put on cathode A glass substrate that (CdO) thin film was deposited on it is placedon glass disc .the distance between the two poles was (2mm) .fig (1) show the non thermal plasma device.

Figure 1: The non-thermal plasma device

2.3.2 X - Ray Diffraction investigation

X-Ray Diffraction measurement was recorded and compared with the JCPDS-International Center for Diffraction Data cards, (using Philips PW 1840) XRD meter systems which record the intensities as a functions Of Bragg's angles. the sources of radiations its Cu(k_{α}) with wavelength λ=1.5406Å, current 30mA and voltage 40kV. the Scanning angle 2θ is vary on the range of(20–80)degree.

The crystallite size all peak was calculated using Scherrer's formula {14}.

$$D = \frac{0.9\,\lambda}{\beta \cos \theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (2)$$

Where λis the X-Ray wavelength, βmust bein radians and θcorrespond to the positions peaks.

2.3.3 Atomic Force Microscopy

The morphological surface of CdO thin film after and before exposure to non –thermal plasma analysis is carried out using atomic force microscope (AA3000 Scanning Probe Microscope SPM. Angstrom Ad-Vance Inc, tip NSC35/AIBS)

2.3.4 Optical Measurement

A double–beamUV-VIS-NIR210A spectrophotometer (VRIAN, made in Australia) was use to determined the transmittances and absorptions of CdO films after and before exposing to non –thermal plasma . transmittance, absorbance Data canbe use to calculated the Absorption coefficient of the film at differents wave lengths, which has been use to determined the band Gap (E_g) by the following equation:{ 13}

$$\alpha\hbar v = A\,(\hbar v - E_g)^{1/2} \ldots\ldots\ldots\ldots\ldots\ldots\ldots (3)$$

Where A is Constant , α the Absorption coefficient s, ħv the incidents photon energy.

3. Results and Discussions

3.1 X-Ray diffractions measurement

The effect non-thermal plasma period between (5-15) min on the films structure has been studied. The X-Ray Diffraction investigate the Structural types ofthe CdO thin filmsprepared by spray pyrolysis technique at substrate temperature 350 ℃ . XRD for the patterns show polycrystalline of cubic CdO structure, It can be clearly seen that all films are preferentially orientated along (111) crystallographic directions, As well as the emergence of four diffraction peaks { (200) , (202) , (311) ,(222) } The XRD patterns for these CdO films are presented in Figure (2), When comparing these Results with JCPDS Card (No:05-0640) it was Found its agrees with the card and with the previous study Despite the different preparation Methods . Also, 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)

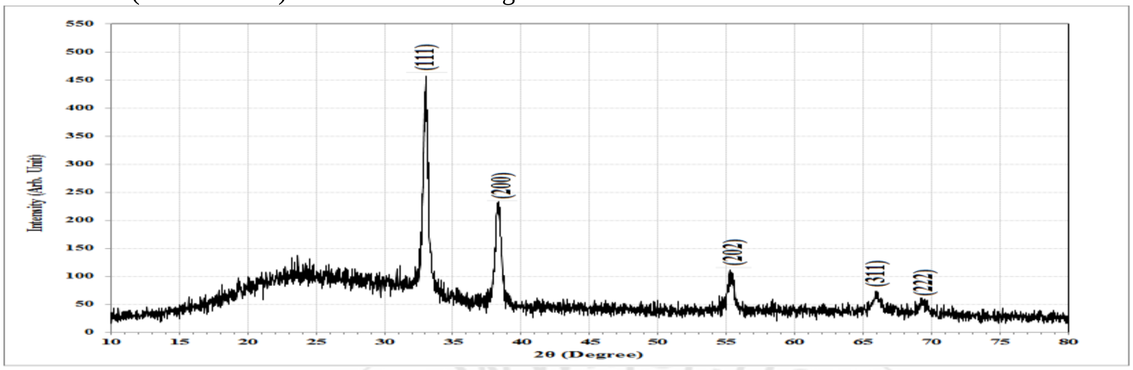

Figure 2: The X-ray diffraction (XRD) patterns of the prepared pure CdO thin film

Table (1-1): The structural parameters

2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl	card No.
33.0289	0.4483	2.7099	18.5	2.7108	(111)	96-900-8610
38.3326	0.4850	2.3463	17.3	2.3477	(200)	96-900-8610
55.3060	0.5200	1.6597	17.2	1.6600	(202)	96-900-8610
65.9357	0.4533	1.4156	20.9	1.4157	(311)	96-900-8610
69.2715	0.3000	1.3553	32.2	1.3554	(222)	96-900-8610

It observed that the XRD diffraction of crystal structure for CdO thin films be affected clearly by the exposing of non-thermal plasma at different times , The patterns reveal the presences of pure poly crystalline CdO Thin film, with a cubic structures and with a preferentials orientations peak for all CdO films, it seen from the fig (3) that the intense of the peaks decreased with increasing time exposure to cold plasma as well as appearance of another new peaks in the diffraction pattern for CdO films , less intense of peaks indicates that increasing of localized state in the optical energy gap consequently the optical energy gap decreased.

For all cadmium oxide thin films it is important to mention that when increase the expose time to non –thermal plasma the grain size (D) decease and the full width at half maximum increased , (D) was calculated from the full width at half maximum (FWHM) β of the preferential orientation diffraction peak by using Scherrer equation, eq. (2). In addition, the various peaks in the figures are listed in Table (1-2) as well as the corresponding values of the inter planar spacing $d_{(hkl)}$ which were calculated.

Table (1-2): The structural parameters of CdO thin films after and before Exposure to non –thermal plasma

CdO	2θ (Deg.)	FWHM (Deg.)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl	card No.
After 5 min	33.1049	0.4497	2.7038	18.44	2.7108	(111)	96-900-8610
	38.3726	0.4497	2.3364	18.72	2.3477	(200)	96-900-8610
	55.3961	0.7709	1.6572	11.64	1.6600	(220)	96-900-8610
	66.1242	0.9636	1.4120	9.84	1.4157	(311)	96-900-8610
	69.5931	0.8994	1.3498	10.76	1.3554	(222)	96-900-8610
After 10 min	33.1048	0.5139	2.7038	16.13	2.7108	(111)	96-900-8610
	38.3726	0.5782	2.3439	14.56	2.3477	(200)	96-900-8610
	55.2677	0.6424	1.6608	13.96	1.6600	(220)	96-900-8610
	65.8672	0.6424	1.4169	14.74	1.4157	(311)	96-900-8610
After 15 min	33.1049	0.6424	2.7038	12.91	2.7108	(111)	96-900-8610
	38.3726	0.7709	2.3439	10.92	2.3477	(200)	96-900-8610
	55.3961	0.6424	1.6572	13.97	1.6600	(220)	96-900-8610

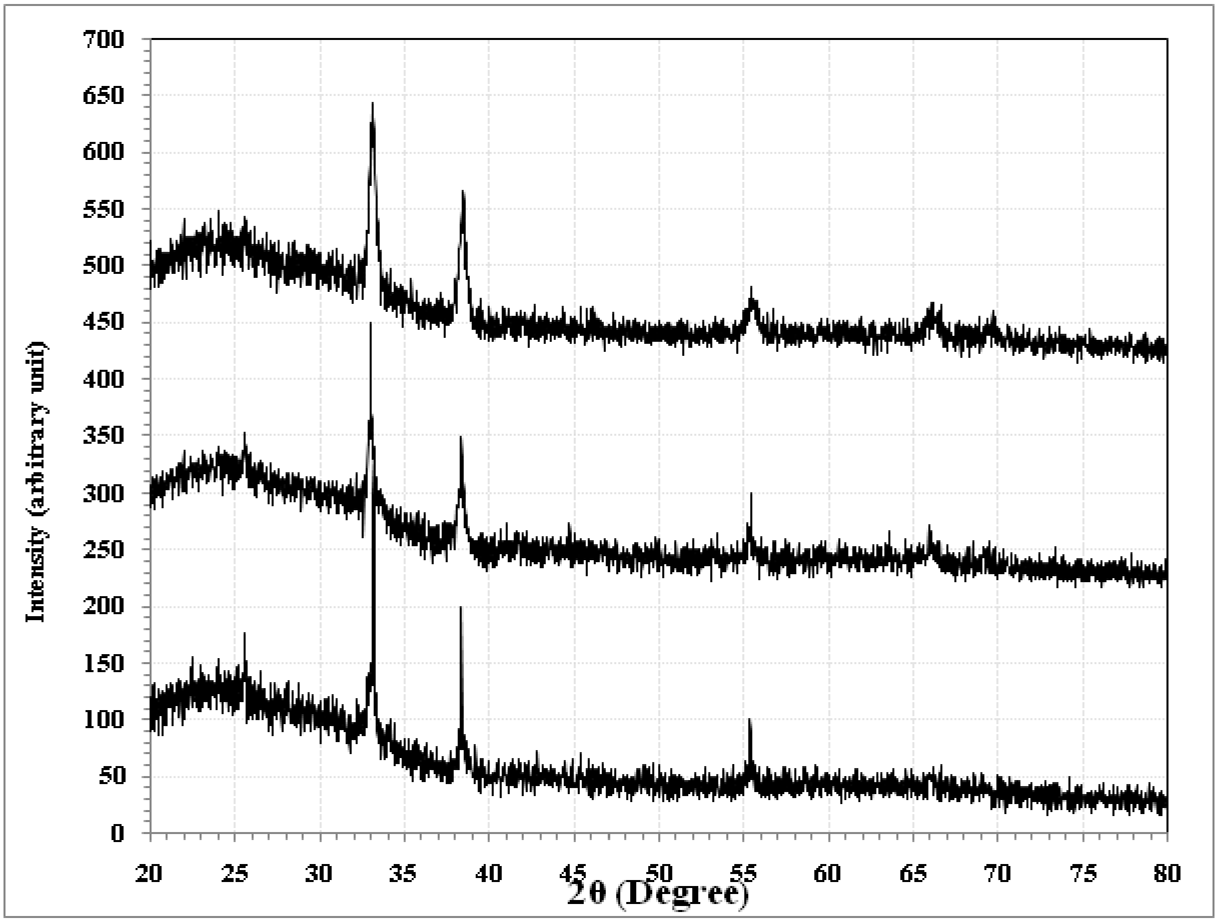

Figure 3: The X-ray diffraction patterns of the prepared films after exposure to non – thermal plasma: (a) CdO after 5 min, (b) after 10 min, (c) after 15 min

3.2 Atomic force microscopy (AFM)

To study the topography of the surface depositions films and its important to used Atomic Force Microscopy, its one of the effectived way for the surfaces analysis dueto its high resolutions and Powerful analysis software, Also we can calculated the degree of (Roughness) and grain size, and gives a picture caption on the rate of distribution of the size of the crystal surfaces {9} . fig (4) show that Analytical CdO thin films topographic images of the two-dimensional surface roughness after and before expousure to non –thermal plasma and it seen that The (Ra) and (Rq) of the pure CdO film are measured to be (11) nm and (12.9) nm respectively. Further, the (Ra) and (Rq) of the samples decrease with increasing the exposure time of non –thermal plasma and thus the Granules surfaces become more uniform These results represented in Table (1-3). The grain sizes values of CdO films are calculated from granularity cumulation distribution. These values indicate that grain size decrease with increasing the exposure time of non –thermal plasma.

Table 7: The roughness(Ra) , root mean square roughness surface (Rq)and grain size (D) of CdO thin film after and before exposure to non –thermal plasma

Material	Ra(nm)	Rq(nm)	D(nm)
CdO	11	12.9	97.46
CdO:After .5 min	1.72	1.99	79.86
CdO: after 10 min	1.03	1.21	64.34
CdO: after 15 min	0.539	0.646	55.62

Figure 4: Two-dimensional AFM images of CdO films after and before exposure to non-thermal plasma

3.3 The Optical Properties

Optical properties has 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{10}. these Properties were important for the understand ofthe mechanisms of electrons transitions between energy band during the measuring of absorption and transmissions of a semiconductors.{11}

The Optical transmittance spectra for CdO thin films was measured in the range from (300–1100) nm at room temperature it seen from the figs (5) which it was clearly noted that the transmissions of all films decreased with increasing of the exposure time of non-thermal plasma ,this behaviors is refer to that increasing the numbers of atom while the exposing time that lead tothe increasing Of the numbers of collisions between incident atoms, which in turn, lead to that increasing of absorptance and decreased transmittances.

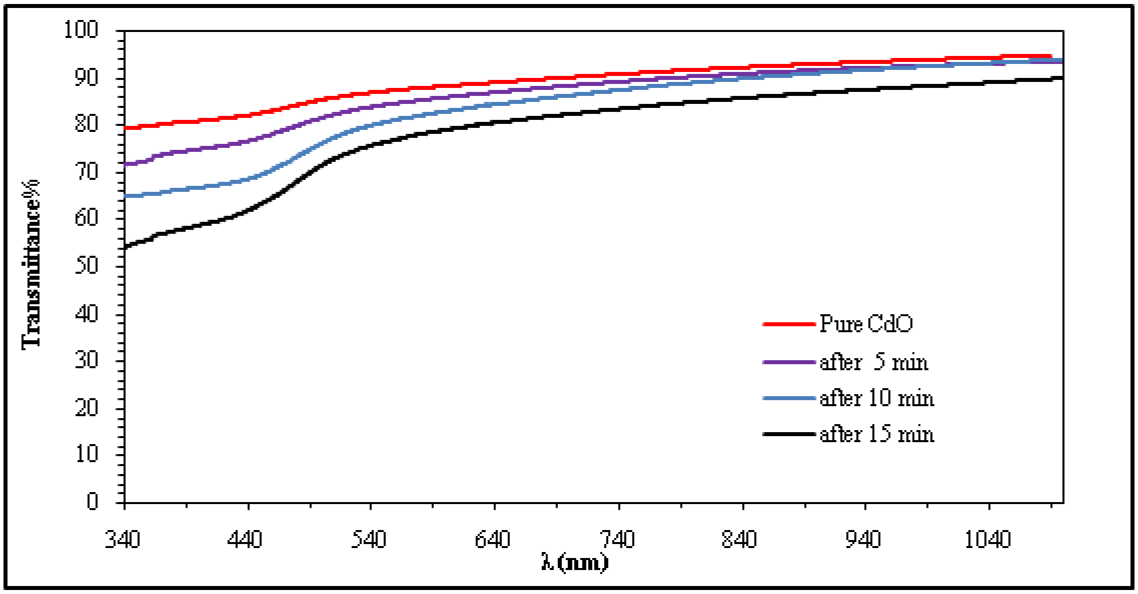

Figure 5: Optical transmittance spectrum of CdO thin film after and before Exposure to non –thermal plasma

The optical absorptions spectrumOf CdO Thin film before and after exposure to non –thermal plasma is shown in the fig (6).It was observed that increases absorption with increased the exposure time of non-thermal plasma ,and with this increment is due to deflection of fundamental absorption edge toward long wavelengths (low Photon energies) This is due to increasing of exposure time of non-thermal plasma has led to an increase in localized state near the conduction band thus, the possibility of absorption Photons with low energy became possible , This confirms the effect of non –thermal plasma In the crystal structure of CdO thin films By create localized state within the energy gap in turn, led to the absorption of low photons energies .{12}

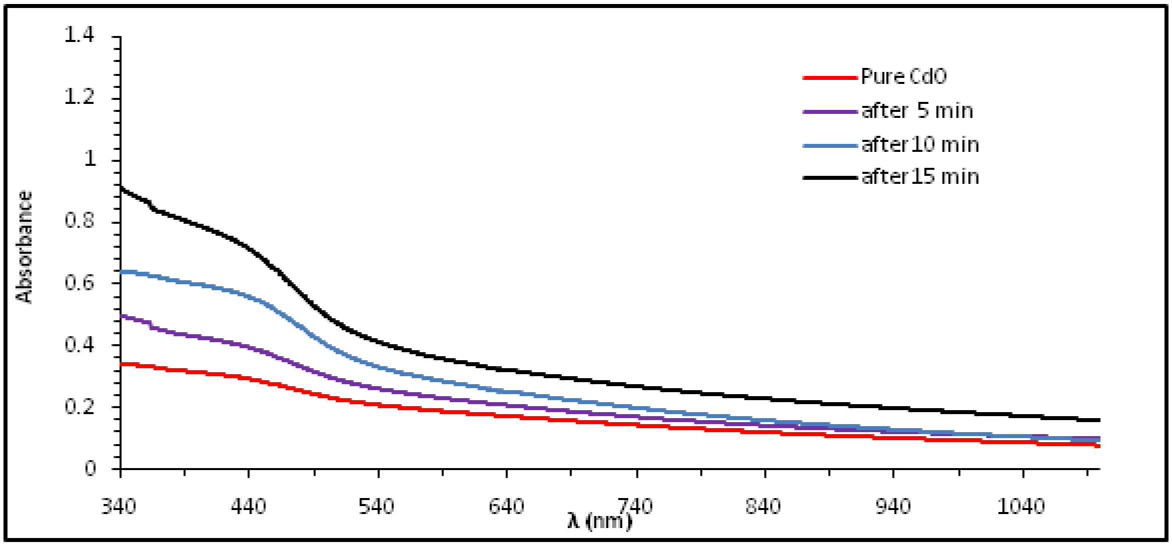

Figure 6: The optical absorbance of CdO thin films after and before Exposure to non –thermal plasma

The optical energy gap values (E_g) for CdO thin films have been determined. A plot of $(\alpha h\nu)^2$ versus hν for cadmium oxide films with (0, ,5 10,15) min exposure time to non thermal plasma is shown in Figure(7).the Optical Energy Gap were estimate by assumed a direct transitions between valence and conduction band, E_g is determine by extrapolated the Straight lines portions, as can be see clearly that the value of energy gap decreases with increase the exposure time of non thermal plasma, this decreasing in the value of energy gap led to removal the Absorption edge towards the low energies. This decrease can be explained that the non –thermal plasma led to increase of the density of localized states in the E_g, near the conduction band, And then absorb photons of low energy and increase in the electronic transmission which causes a shift to lower values of energy gap. this reducing is importance because of easily transmission of electrons from valance band to the conduction band which make CdO thin films uses in various electronic applications.

These results indicate that the allowed direct transition is the dominant in CdO thin films. Table (1-4) shows the value of optical energy gap after and before exposures to non-thermal plasma.

Table (1-4): The value of optical energy gap after and before exposure to non –thermal plasma

Time exposure to non-thermal plasma	The optical energy gap E_g(eV)
CdO pure	2.260
After 5 min	2.240
After 10 min	2.230
After 15 min	2.210

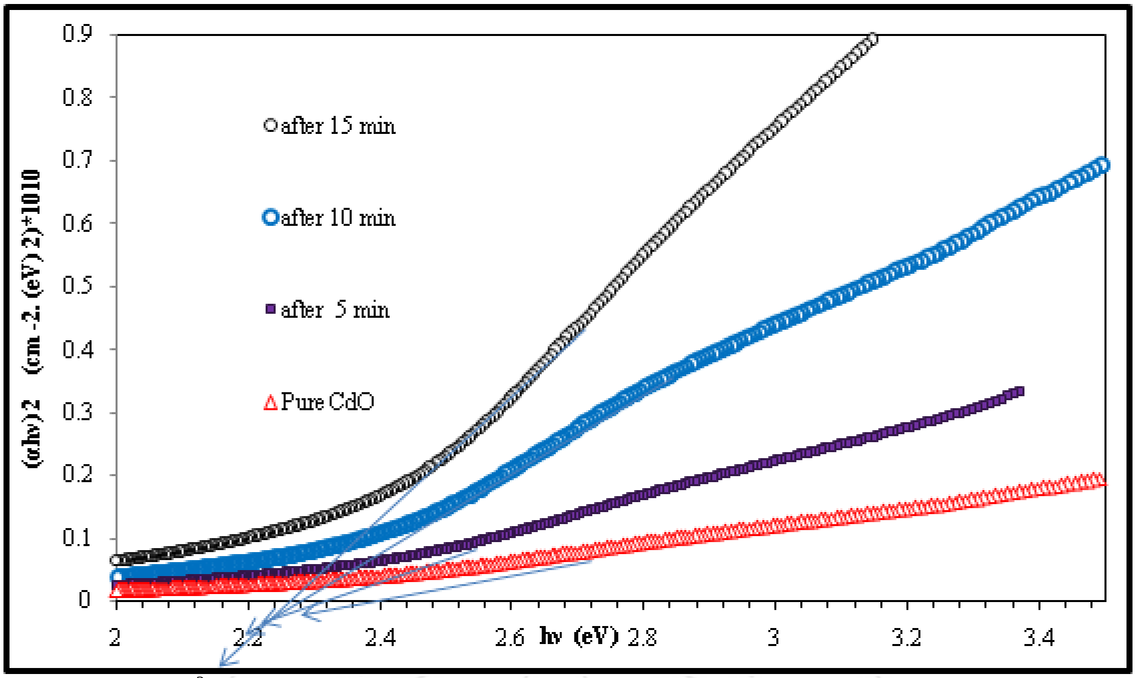

Figure 7: The $(\alpha h\nu)^2$ versus photons energies (hν) for CdO after and before Exposure to non –thermal plasma

The Absorption coefficients α were determine from that regions of highly absorptions atthe fundamentals Absorption edges of the films, the value of α for all thin films are found to be greater than 10^4 cm^{-1} in the visible region which mean that the CdO thin films have a direct optical energy gap so the value of r is equal to 1/2. It notes from fig (8) that the absorption coefficient α increase with increase the exposure time of non-thermal plasma.

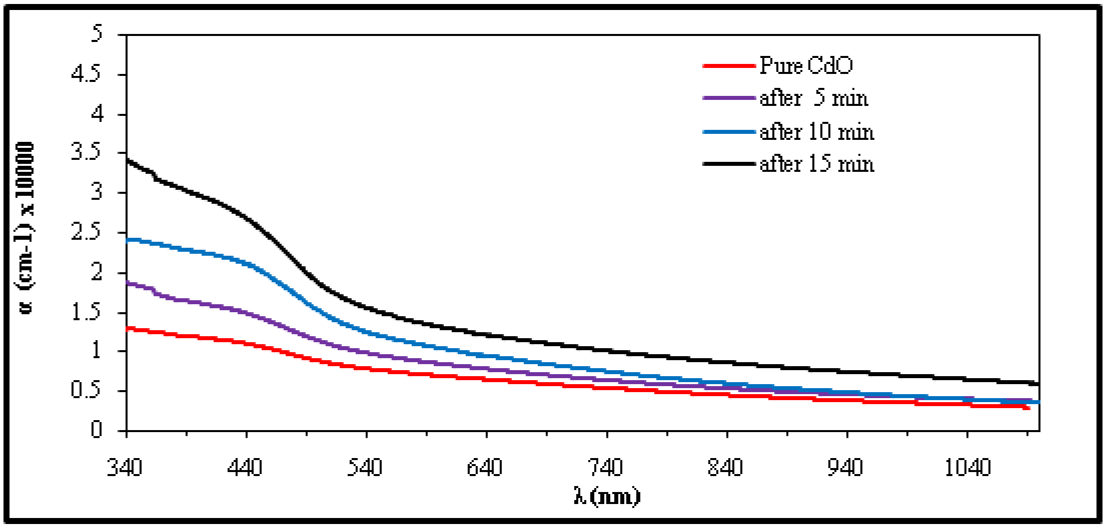

Figure 8: The variations of the Absorption coefficients with wavelength for CdO thin film after and before Exposure to non –thermal plasma

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 (9) shows the variations of the Refractive Index as a functions Of the wavelength for CdO thin films. It indicates that the refractive index increases with increasing of the exposure time of non thermal plasma , The increase is due to higher packing density and the change in crystalline structure, this increase due to the improvement of growth crystalline .

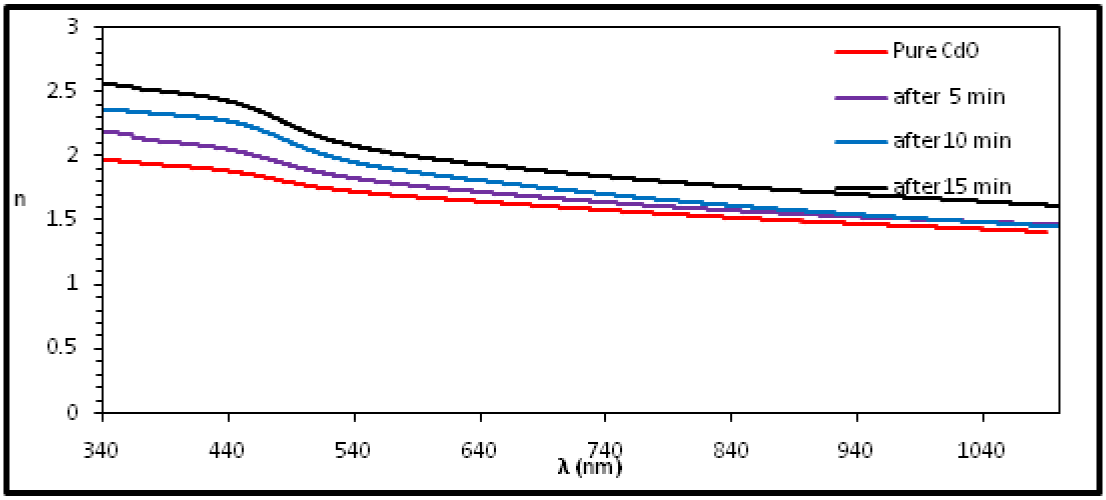

Figure 7: Variation of refractive index with wavelength of CdO films after and before Exposure to non –thermal plasma

4. Conclusion

Cadmiumm Oxide thin film was deposited Spray Pyrolysis Technique at a substrates temperatures 0f 350℃ . the thickness of the films about 180-190 mM were calculated byGravimetric method and interference fringe.CdO thin films exposure to non-thermal plasma period between (5 - 15) min Respectively. AFM images show that the averaged roughness and Root Mean Square roughness Surface of the film decrease with increasing the exposure time of non –thermal plasma. the optical properties measure by (UV-VIS) shows the transmissions of all films decreased with increase the Exposure time of non-thermal plasma . it was notes from study that increase absorption with increase the Exposure time of non-thermal plasma ,and with This increment there is a deflection of fundamental absorption edge Toward long wavelengths (low Photon energies). As can be seen clearly that the optical band gap of *CdO* thin films decreases with increase the exposure time of non thermal plasma, this decreasing in the value of energy gap led to removal the Absorption edge towards the low energies.. Poly crystalline nature and cubic structure of CdO films after and before exposure to non thermal plasma were confirmed by XRD, Its can been clear see the all film were Preferentially orientation alongs(111) crystallographics direction and the intense of Preferential orientations of the peaks decreased with increasing time exposure to cold plasma as well as appearance of another new peaks in the diffraction pattern for CdO thin film.

The Structural parameter Such As diffractions angles , lattice space, Full widths at half maximum, And that phases identify alongs with (hkl) planes was evaluate from those spectrum and present on table (1.2) .

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