Structural and Optical properties of Some Metals Doped CdO Synthesized by Sol-Gel Method

L.A. Wahab[a], H.A. Zayed[b], I.S. Yahia[c], N.M. Yousif[a*]

[a]*Solid State physics and Accelerators Department in National Center for Radiation Research and Technology, Nasr City, Cairo, Egypt.*

[b] *PhysicsDepartment in Faculty of women for Art, Sciences, and Education , Ain Shams University, Heliopolis ,Cairo, Egypt ..*

[c]*Department of Physics, Faculty of Science, King Khalid University, P.O. Box 9004, Abha, Saudi Arabia*

Abstract:

Nanoparticles with crystallite size in the range 8.23-27.88 nm of transition metals (TM= Cr, Cu, Co, Ni, Mn, and Fe) doped (CdO) films were deposited by the sol-gel spin coating method. The strain, the grain size, lattice parameters and dislocation density were estimated from the XRD patterns. The calculated band gap for CdO is 2.302 eV and is increased with doping.

Keywords:Metal Oxide Semiconductors, TM- doped CdO, nano-structure, XRD, Spectrophotometer, Optical constants.

***Permanent address*:** thermal and magnetic lab. NCRRT,AEA, Cairo, Egypt.

Introduction:-

The metal oxide semiconductor materials have attracted much attention owing to their potential applications in electronic and photovoltaic devices. CdO is an n-type semiconductor with a rock-salt crystal structure (FCC) and possesses a direct band gap of~ 2.2 eV [**Ortega, M., etal., 1765**]. High electrical conductivity and high optical transmittance in the visible region of the solar spectrum along with a moderate refractive index of CdO make it useful for various applications such as solar cells, transparent electrodes, phototransistors, photodiodes, gas sensors, etc [Ferro,R., etal., 2000; Subramanyam, T.K., etal., 1998; Muralia,K.R.,etal.,2010].

* **Corresponding author:**

N.M.Yousif(NashwaYousif, yousif_nashwa@yahoo.com)

The electrical and optical properties of CdO can be tuned through doping with different metals [**Deckate, RJ., etal.,2008**].

A variety of techniques such as sol-gel [**Carballedo-Galicia, DM., etal., 2000**], spray pyrolysis [**Lokhande, B.J., etal., 2001**] , sputtering method [**Mastsuura,N., etal., 1997**], chemical bath deposition (CBD) [**Ortega, M., etal., 1765**], Langmuir-Blodgett (LB) deposition [**Carballedo-Galicia, DM., etal., 2000**], activated reactive evaporation [**Ramakrishna Reddy, K.T., 1998**] and metal organic chemical vapour deposition (MOCVD) [**Zhiyong Zhao, etal., 2002**] have been employed to prepare CdO films.

The sol-gel method has several advantages because of its simplicity, easy control of the film composition, safety, low cost of the apparatus and raw materials [**Maity, R., etal., 2006**].

In an effort to investigate the enhancement of CdO properties for more applications, CdO was doped with transition metal ions with ionic radii smaller than Cd^{2+} and deposited by the sol-gel spin coating method. This study concerned with the effect of Cr, Cu,Co,Ni,Mn and Fe doping on the structural and optical parameters of CdO.

Experimental details:

Thin films of CdO and (Cu, Mn, Cr, Ni, Co, Fe) doped CdO were fabricated using the sol gel technique. Cadmium acetate, copper acetate, Manganese acetate, chromium Chloride, Nickel acetate, Cobalt acetate and Iron chloride, 2-metoxyethanol and diethanolamine. In a typical synthesis, 0.5 M of cadmium acetate was slowly dissolved in 2-metoxyethanol followed by addition of diethanolamine were used to prepare CdO films. For doping with (Cu, Co, Ni, Fe, Mn, and Cr) to CdO, there salts were added in the above mixture. The prepared mixtures were stirred using a magnetic stirrer at 60$^{\circ}C$ for about 2h to obtain clear homogeneous solution and then the solution was kept for aging for 18h prior to film deposition. The pure and metals (Cu, Co, Ni, Fe, Mn, and Cr) doped CdO films were deposited on microscopy glasses by the sol-gel spin coating followed by heating at 150 $^{\circ}C$ for 10 min to evaporate the solvent and remove organic residuals. The prepared undoped and doped CdO films were annealed at 400 $^{\circ}C$ for 4 hs in furnace. The transmittance and absorbance properties of the films were taken by spectrophotometer UV/VIS V-670 wavelength range 2600-200 nm. X-ray diffraction (XRD) patterns were obtained with XRD-6000 Shimadzu X-ray diffractometer using CuK_{α} radiation (λ=1.54059A^{o}) in the range 2 between (4 and 50 $^{\circ}$).

Results and discussion:

XRD patterns of the undoped and doped of the investigated CdO films are shown in Fig.(1). The patterns indicate that all of the investigated films have a polycrystalline structure.

The interplanar spacing (d_{hkl}) data of the observed peaks and its relative I/I_o for the investigated films were compared with JCPDs cards to obtain the system configuration (table (1)).

The grain size, strain, lattice parameter, dislocation density and texture coefficient were estimated from the XRD pattern. The average grain size and strain for the films can be determined using the equation [**Gurumurugan, K., 1995**]:

$$\frac{\beta \cos\theta}{\lambda} = \frac{1}{L} + \frac{\varepsilon \sin\theta}{\lambda} \qquad (1)$$

where β= FWHW and θ the Bragg angle, D grain size and ε is the strain. The plot of (β cosθ/λ) vs (sin θ/λ) for the various reflection planes was plotted. The D and ε values were determined from the intercept and slope of this graph and given in table (1). The table illustrates that grain size of the investigated thin films are in the nano scale. The grain size of CdO film increased with doping metals.

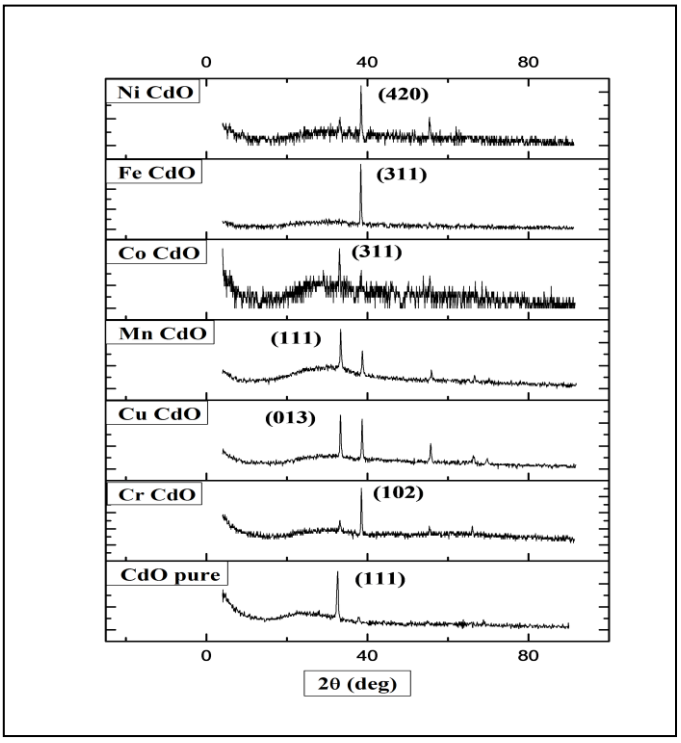


Fig.(1) XRD patterns of undoped and doped Cdo.

The dislocation density values were calculated using the standard relation:

$$\delta = \frac{n}{L^2} \qquad (2)$$

Where (a) is the lattice parameter and (D) is the grain size. The lattice parameter (a) for the investigated films was calculated using the unit cell programme [**Holland TJB and RedfernSAT, 1997**]. Table (1) illustrates the good agreement between the calculated lattice

parameter ($\mathbf{a_{exp}}$) values and the standard ($\mathbf{a_s}$). The values of dislocation density are given in table (1).

Table (1) the values of Grain Size, Strain, Dislocation density, and Lattice Parameters of pure and doped CdO.

sample	Grain Size (D) , nm	Strain (ε)	Dilocation Density (δ)	a_{exp}	a_s	Card No.
CdO pure	8.23	$4.21*10^{-3}$	$1.476*10^{-2}$	4.6831	4.695	75-0594 **[Cimino, A., etal., 1960]**
Co CdO	12.03	$2.879*10^{-3}$	$6.909*10^{-3}$	8.5257	8.54	52-1798**[Vasambekar,R., 2001]**
MnCdO	13.39	$2.586*10^{-3}$	$5.57*10^{-3}$	4.6461	4.659	89-5995 **[Kusigerski, V., etal., 1996]**
Ni CdO	17.005	$2.037*10^{-3}$	$3.458*10^{-3}$	10.3613	10.43	02-0976 **[Ferrai, etal., 1935]**
Cr CdO	17.29	$2.004*10^{-3}$	$3.345*10^{-3}$	3.016	2.974	89-6743 **[Crotlaz, O., etal., 1996]**
Cu CdO	18.26	$1.897*10^{-3}$	$2.9992*10^{-3}$	3.825	3.8	45-0554 **[Qian, Y., etal., 1994]**
Fe CdO	27.88	$1.24*10^{-3}$	$1.286*10^{-3}$	8.6656	8.708	79-1155 **[Arean, C.O., etal., 1988]**

It is clear from the table that, as the values of the grain size, increases the values of strain and dislocation density increase for the investigated films.

Thus doping of CdO with metallic ions of smaller radius (80nm,83nm,78nm74.5nm,60nm,and73nm) like ($Cr^{2+,}Mn^{2+,}Fe^{2+,}Co^{2+,}Ni^{2+}$and Cu^{2+}) than Cd^{2+} (95nm) can control crystal size[**Bhatli, K.P., etal., 2005; Ekambaram, S., etal., 2006; Weast, R.C., 1975; Volbers, N, etal., 2007; Li,L.,etal., 2009**].

Fig.(2,a) shows the transmittance spectra of pure CdO film and doped films. The figure illustrates that the films have nearly 70% transmittance in the optical region. The transmittance of CdO film decreases by doping. This decrease in transmittance may be due to the absorbance increase (fig2b) by free carriers. The optical absorption edge was analyzed by the following relationship [**Pankova, J.I., 1971**]

$$\alpha h\upsilon = A\,(h\,\upsilon - E_g)^{n} \qquad (4)$$

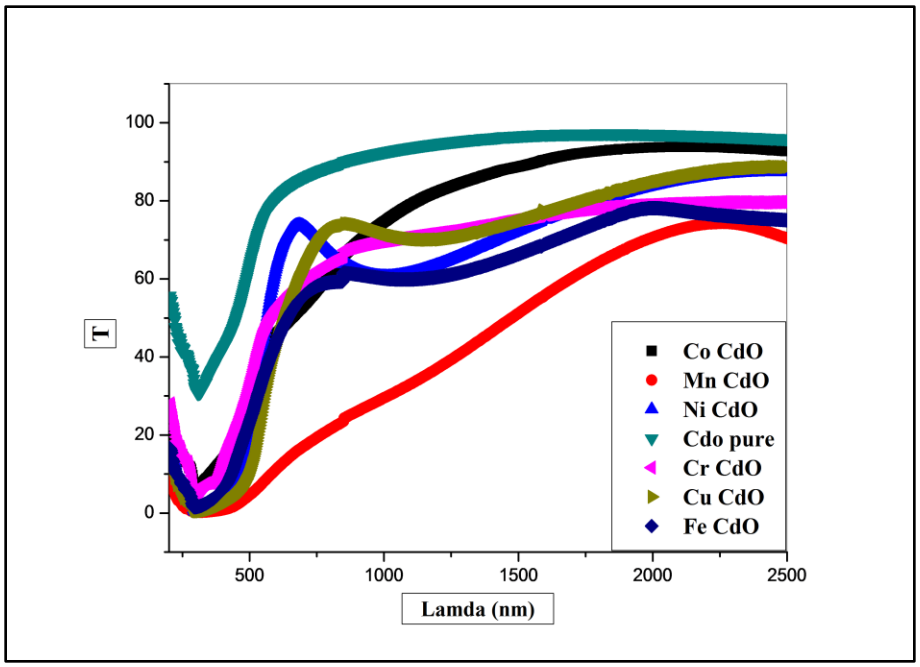
Where A is a constant, h υ is the photon energy and E_g is the optical band gap. Fig (3) shows the plots of $(\alpha h\upsilon)^2$ vs. hυ, the values of E_g in table (2) indicate that E_g for CdO increases with the addition of TM. This effect is frequently observed in n-type semiconductors. The change of

carrier concentration in doped thin films cause the Fermi level move into the conduction band. The filling of the conduction band by electrons generally result in blue shift in the near band edge emission. The shifting in the optical band gap of any material, usually semiconductors, is known as Bursteing-Moss shift due to doping effect. This blue shift may be due to the increase in grain size which leads to widening of the band gap.

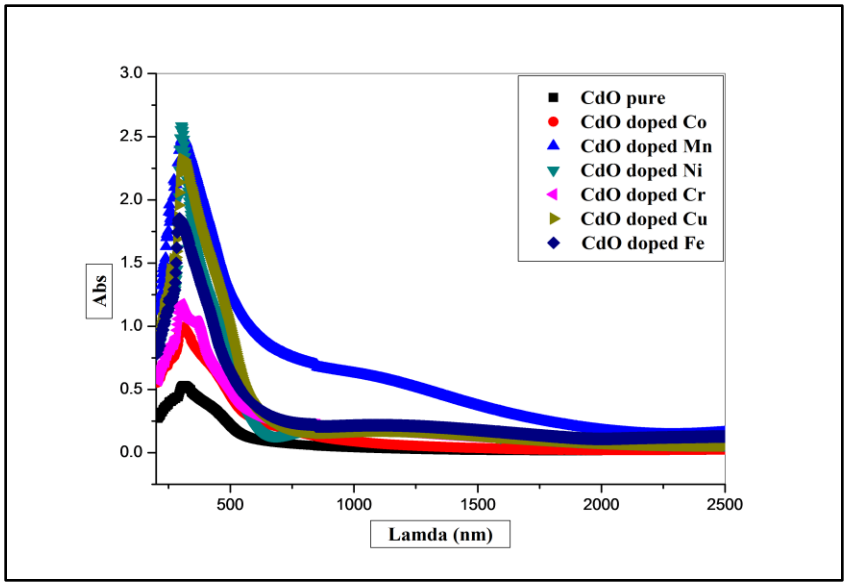
Spectral change in the optical absorption near the band edge is characterized by an α (υ) that increases exponentially with hυ , obeying the exponential relation:

$$\alpha(\upsilon) = \alpha_0 \exp(h\upsilon/E_s) \qquad (5)$$

where α_0 is a constant and E_s is interpreted as the width of tails of the localized states in the gap. It represents the degree of disorder [**Mustafa Öztas, etal., 2008**]. Fig (4) illustrates log α as a function of hυ. E_s was calculated and given in table (2). It is observed that the addition of TM to CdO decrease E_s. Since E_s represents the degree of disorder, adding TM to CdO decrease the disorder. The decrease of disorder is responsible for the increase of the optical gap.



(a)Transmittance of undoped and doped CdO



(b)Absorbance of undoped and doped CdO

Fig. (2(a,b)) Transmittance and Absorbance and of undoped and doped CdO samples.

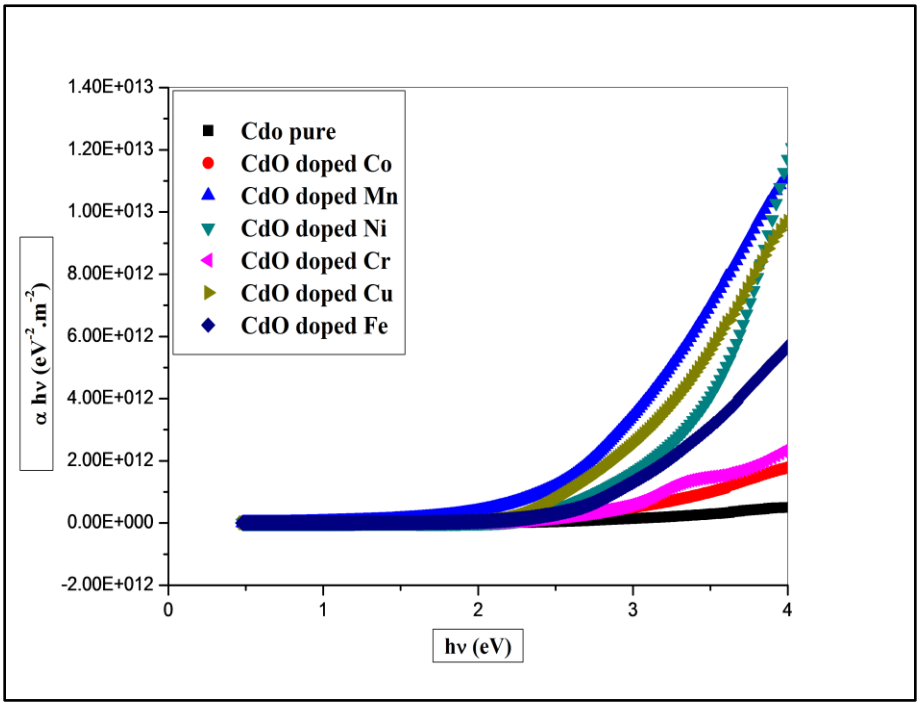


Fig. (3) The plots of $(\alpha h\upsilon)^2$vs. photon energy of the undoped and doped CdO.

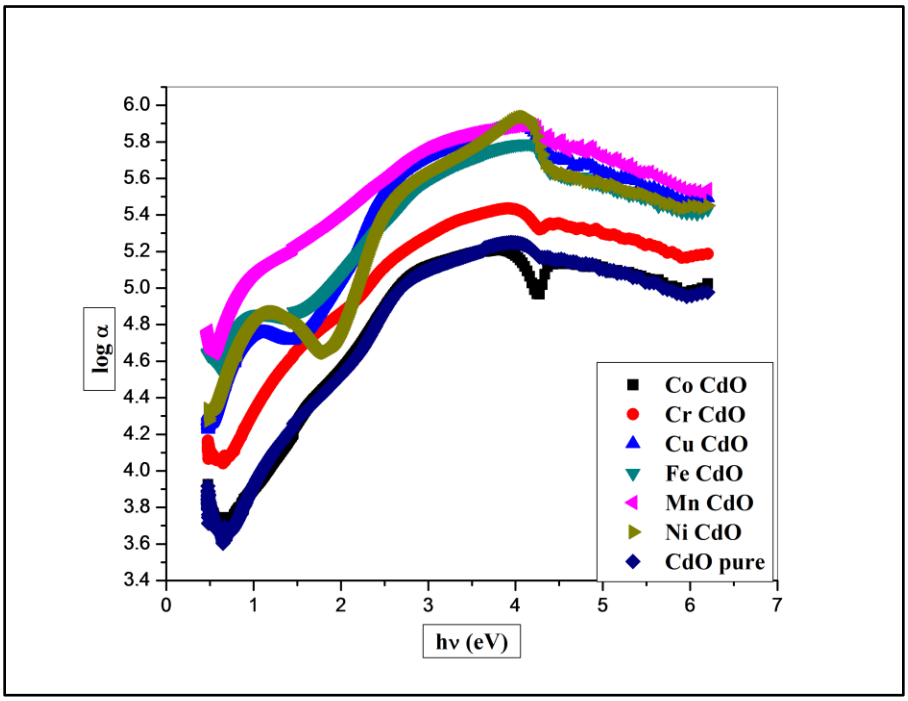


Fig. (4) Log α as a function of photon energy (hυ)

Table (2) illustrates the values of band gap energy (E_g) and the width of tails of the localized states in the gap.

Sample	E_g (eV)	E_s(eV)	E_{opt} (eV)
CdO	2.33	1.865	1.98
Ni CdO	3.016	1.112	1.91
Co CdO	2.56	1.62	1.72
Cr CdO	2.53	1.66	1.11
Cu CdO	2.489	0.9515	1.679
Fe CdO	2.57	1.85	1.46
MnCdO	2.377	0.9227	1.34

The refractive index dispersion plays an important role in the research for optical materials; it is a significant factor in optical communication and designing devices for spectral dispersion. The refractive index of the films was calculated according to the relation [**Subrahamanyam, N.A., 1997**],

$$n = (1+R)/(1-R) + (4R/(1-R)^2)^{1/2} - K^2 \qquad (8)$$

where k (k= αλ/4Π) is the extinction coefficient. Figure (5) gives the variation of refractive index with the wavelength.

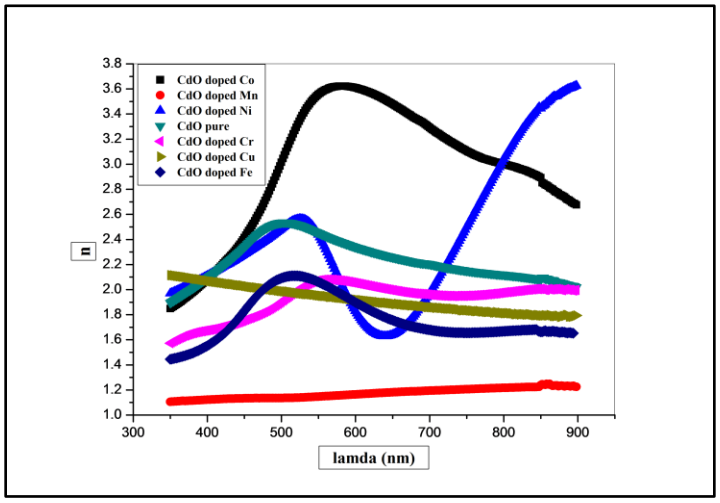


Fig.(5) the refractive index dependence of wavelength for the investigated films

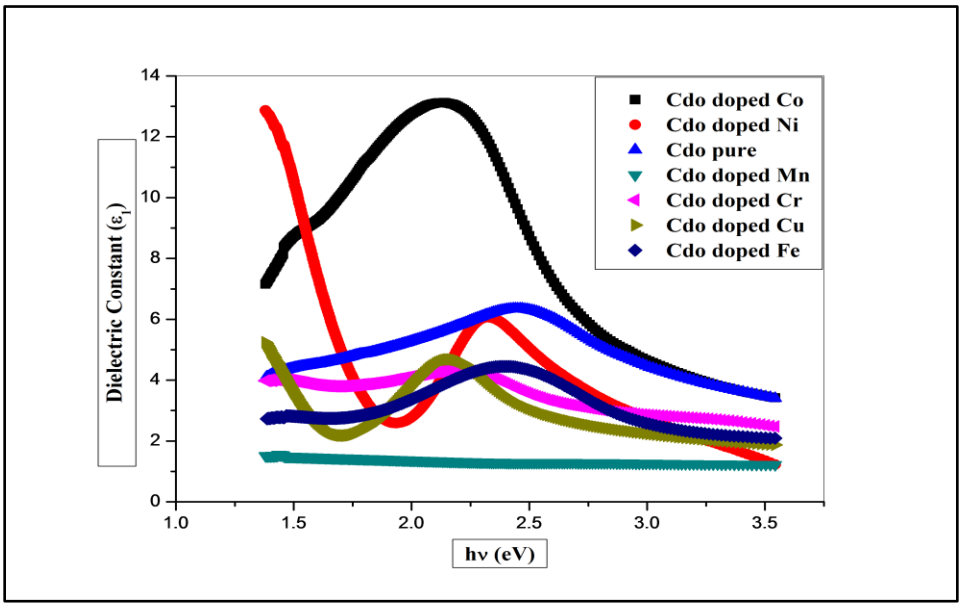
Regarding CdO, Cr, Co and Fe, n is observed to increase as hυ increases to a point near to the value of E_{opt}, where it turns over and begins to decrease. In case of Ni and Cu n is observed to decrease to a point lower than E_{opt}, where it turns over and begins to increase. Regarding Mn, n is observed to decrease with energy.

The fundamental electron excitation spectrum of the films was described by means of a frequency dependent of the complex electronic dielectric constant. Real and imaginary parts of the dielectric constant are related to the n and k values. The ε_1 and ε_2 values were calculated using the formula [**Moss, T.S. 1973**],

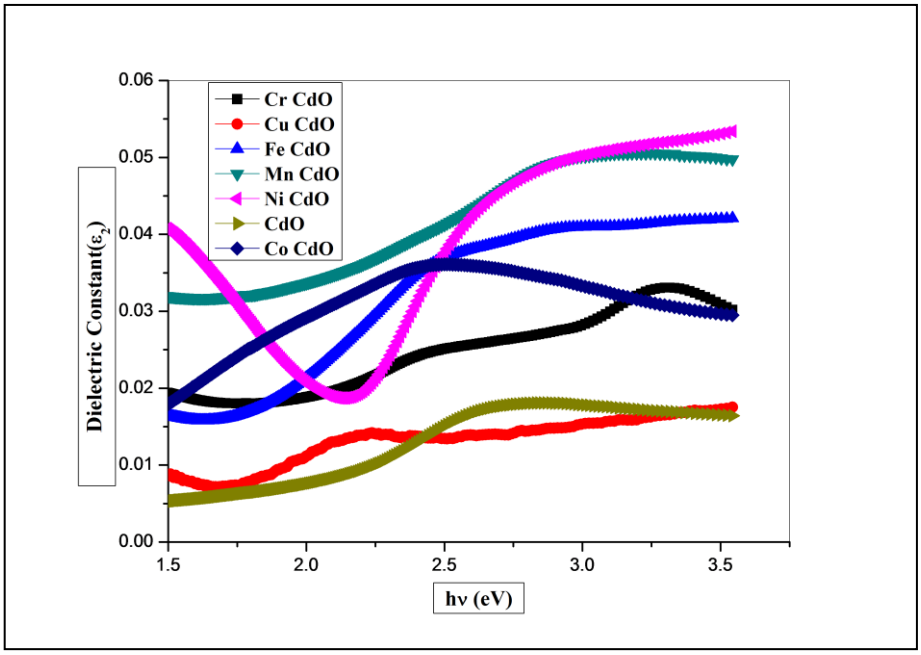
$$\varepsilon_1 = n^2 - k^2 \qquad (10)$$

$$\varepsilon_2 = 2nk \qquad (11)$$

Fig.6 (a,b) shows ε_1 and ε_2 values dependence on the photon energy (hυ)



(a)



(b)

Fig.(6) (a) the dielectric constant (ε_1) and (b) the dielectric loss (ε_2) dependence on the photon energy ($h\upsilon$).

From this figure clears the dielectric constant decreases with increasing photon From energy then increases and then decreases again with further increasing photon energy, except in case of CdO doped Co the dielectric constant increases then decreases with increasing of photon energy. However, the dielectric loss has constant values with increasing photon energy, but in case of CdO pure the dielectric loss increases with increasing photon energy, and except in case of CdO doped Ni dielectric loss decreases then increases with increasing photon energy.

The optical conductivity σ_{opt} can be calculated by using the absorption coefficient α as in the following equation [**Pankova, J.I., 1975**]:

$$\sigma_{opt} = \frac{\alpha n c}{4\pi} \qquad (12)$$

where n is the refractive index and c is the velocity of light. Fig .(7) shows the variation of the optical conductivity as a function of photon energy .it is clear that the optical conductivity increases with increasing photon energy this may be due to the excitation of electrons by photon energy, and the optical conductivity increases with doping.

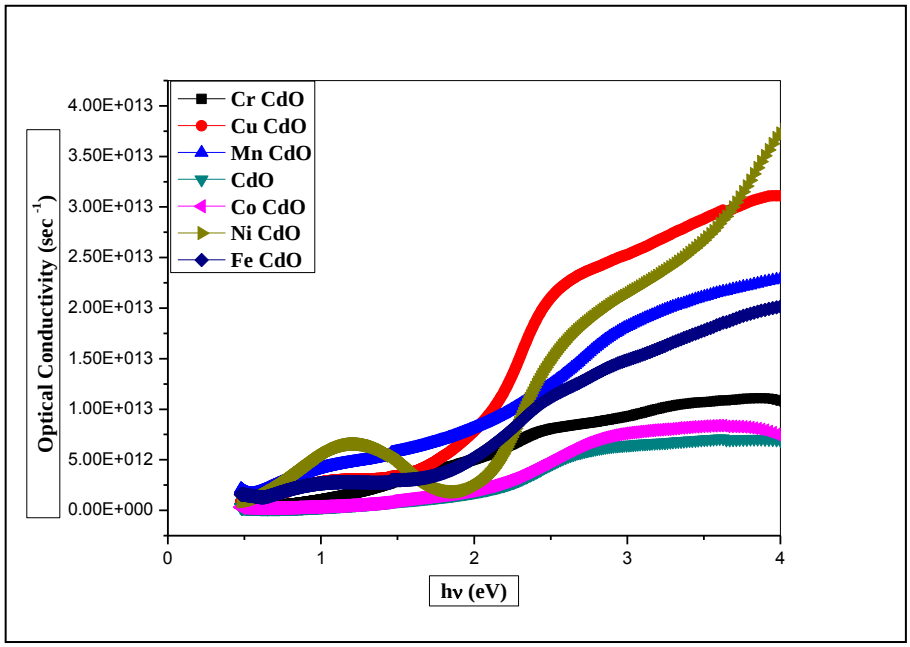


Fig. (7) The optical conductivity dependence on the photon energy for the investigated thin films.

Conclusion

Transition metals (Cr, Cu, Co, Ni, Mn, and Fe) doped CdO thin films were deposited on glass substrates using sol-gel spin coating method. X-ray diffraction patterns reveal the polycrtstalline structure of the prepared films, the obtained value of the grain size of CdO increased with doping with TM.

Reference:-

Arean, C.Oetal.,*J.Solid State Chem*., 77, 272 (1988).

Barret, C.,Massalski,T.B., *Structure of Metals, Pergamon,* Oxford, P. 1923(1980).

Bhatti K. P., Chaudhary S., Pandya D.K. and Kashyap S.C., , "On the room- temperature ferromagnetism in $(ZnO)_{0.98}(Mn)_{0.02}$ O_2". *Solid state Commun*.136, 384-388, (2005).

Carballeda-Galicia DM., Castanedo-Perez R., Jimenez-Sandoval O., Jimenez-Sandoval S., Torres-Delgado G., Zuniga-Romero CI., , High transmittance CdO thin films obtained by the sol-gel method. *Thin Solid Films* 371,105, (2000).

Cimino A., Marezio M., Lattice parameter and defect structure of cadmium oxide containing foreign atoms. *J. phys.Chem.Solids*, 17, 57, (1960).

Crottaz O.,Kubel F., Kristallogr Z.,Crystal structure of copper (I) chromium (III) oxide, 2H-CuCrO2.*American Journal of Nano Research and Application*211, 481,(1996).

DeokateRJ.,Pawar SM., Moholkar AV., Sawant VS., Pawar CA., Bhosale CH., Rajpure KY., Spray deposition of highly transparent fluorine doped cadmium oxide thin films. *Appl.Surf.Sci*,254 , 2187, (2008).

Ekambaram S., Yoichi Iikubo, Akihiko Kudo, *J.Alloys& compounds*, 433, 237 (2006).

Ferrai, Colla, Gazz., American Mineralogist Crystal Structure Database. *Chim.Ital*. 65, 815, (1935).

Ferro R., Rodriguez J.A., Influence of F-doping on the transmittance and electron affinity of CdO thin films suitable for solar cells technology.*Solar Energy Mater.and Solar Cells* 64, 363,(2000).

Gurumurugan K., Mangalaraj D., NarayandassSa.K., Structural characterization of cadmium oxide thin films deposited by spray pyrolysisOriginal Research Article.*Journal of Crystal Growth*, Volume 147, Issues 3–4, 1 February, Pages 355-360,(1995).

Holland TJB and Redfern SAT, " the unit cell refinement from powder diffraction data: the use of regression diagnostic, 1997.

Kusigerski V., Spasojevic V., Synthesis and some physical properties of the diluted magnetic semiconductor Cd1-xMnxO.*J. phys., Cadens Matter*, 8, 10581, (1996).

Li L., Wang W., Lui H., Lui X., Song Q., RenS., , First principles calculations of electronic band structure and optical properties of Cr-doped ZnO, *The Journal of Physical Chemistry C* , 113 (19), 8460-4, (2009).

Lokhande B.J., Uplane M.D., Effect of deposition temperature on spray deposited cadmium oxide films. *Mater. Res. Bull.*36,439, (2001).

Matsuura N., Johnson D.J., Amm D.T., Fabrication of cadmium oxide thin films using the Langmuir-Blodgett deposition techniqueOriginal Research Article.*Thin Solid Films*, Volume 295, Issues 1–2, 28 February, Pages 260-265,(1997).

Maity R., Chattopadhyay K.K., Synthesis and characterization of aluminum-doped CdO thin films by sol–gel process. *Sol. Energ. Mater.Sol. Cell* 90, 597, (2006).

Moss T.S., Burrell G.J., Ellis B., Semiconductor *Opto-Electronics*, Wiley, New York, (1973).

Muralia K.R., Kalaivananb A., Perumalc S., NeelakandaN. Pillaic, Sol–gel dip coated CdO:Al films. *Journal of Alloys and Compounds*503, 350, (2010).

Mustafa Öztas, MetinBedir, Thickness dependence of structural, electrical and optical properties of sprayed ZnO:CufilmsOriginal Research Article. Thin Solid Films, Volume 516, Issue 8, 29 February, Pages 1703-1709, (2008).

Ortega M., Santana G., A. Moroles A. Acevedo, Optoelectronic properties of CdO/Si photodetectors.*Solid State Electron*44, 1765, (2000).

Pankova, J.I., Optical Processes in Semiconductors, *Dover Publications Inc*., New York, P.91, (1975).

Pankova J.I., Optical Processes in Semiconductors, *Prentice-Hall Inc.*, Englewoord Cliffs, NJ, (1971).

Qian,Y., et al., Univ. Of Science's Technology of China, Hefi, Anhui, People's Repulic of China, *Private Communication* (1994).

Ramakrishna Reddy K.T., Sravani C., Miles R. W., Characterisation of CdO thin films deposited by activated reactive evaporation. *J. Cryst. Growth*, 184-185, 1031, (1998).

Subrahamanyam N.A., A text book of Optics, 9 ed.: Brj. Laboratory, Delhi, India,(1977).

Subramanyam T.K., Uhanna S., Srinivasula B. Naidu, Preparation and characterization of CdO films deposited by dc magnetron reactive sputtering.*Mater.Latt*.35,214, (1998).

Vasambekar P., Dept. of Electronics, Shivioji Univ., Kolhpur, India, *Private Communication*, (2001).

Volbers N., Zhou H., Knies C., Pfisterer D., Sann J., Hofmann D., Meyer B.K., , synthesis and characterization of ZnO: CO nanoparticles. *Applied physics A: Materials Science & Processing* 88 (1), 153-5, (2007).

Weast R.C., Handbook of Chemistry and Physics, 56thedn, CRC Press, Cleveland, Cleveland, 19760, 1975.

Zhiyong Zhao, Morel D.L., Ferekides C.S., Electrical and optical properties of tin-doped CdO films deposited by atmospheric metal organic chemical vapor deposition Original Research Article. *Thin Solid Films Volume* 413, Issues 1–2, 24 June, Pages 203-211, 2002.

الملخص العربي

دراسة الخواص البلورية والضوئية لاكاسيد الكاديوم المطعمة ببعض العناصر الانتقالية المحضرة بطريقة السول جل

ا.د. لبني علي عبد الوهاب1 - حمدية عبد الحميد زايد2 - ابراهيم سيد يحيي3 - نشوي محمد محمود يوسف1

1- قسم فيزياء الجوامد والمعجلات الألكترونية- بالمركز القومي لبحوث وتكنولوجيا الأشعاع-هيئة الطاقة الذرية
2- قسم الفيزياء بكلية البنات للاداب والعلوم والتربية- جامعةعين شمس
3- قسم الفيزياء بكلية العلوم – جامعة الملك خالد- ابها- المملكة العربية السعودية.

اكاسيد الكاديوم النانومترية المطعمة ببعض العناصر الأنتقالية (الكروم ، النحاس، الحديد ، النيكل، المنجنيز، الكوبالت) المحضرة علي شكل الأغشية الرقيقة المحضرة بطريقة السول جل فوجد ان حجم البلورات يترواح بين 8.23 حتي 27.88 نانوميتر. و تم حساب كلا من حجم البلورات والأجهاد وابعاد البلورة وكتافة الشوائب من رسمة حيود الأشعة السينية. وتم حساب قيمة الفجوة وجد انها في حدود 2.302 الكترون فولت لاكسيد الكاديوم النقي و تزيد قيمة الفجوة مع اضافة العناصر الانتقالية.