Structural and Optical properties of CdO doped TiO_2 thin films prepared by Pulsed Laser Deposition

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Abstract

TiO_2 thin films have been deposited at room temperature with different concentration of CdO of x= (0.0, 0.05, 0.1, 0.15 and 0.2) wt. % onto glass substrates by pulsed laser deposition (PLD) technique using Nd-YAG laser with λ=1064nm, energy=800mJ and number of shots=500. The structural, morphological and optical characterizations of as- deposited films were carried out using X-ray diffraction (XRD), atomic force microscopy (AFM), and UV–vis transmittance spectroscopy. The Effect of CdO content on these properties was investigated. Characterizations by X-ray diffraction show a polycrystalline film, with tetragonal structure and formation of Rutile phase and many peaks (110), (101), (111) and (211) were appear. In addition, AFM investigation shows no cracks in the formed layer. The optical properties concerning the absorption and transmission spectra were studied for the prepared thin films using an ultraviolet–visible near-infrared spectrophotometer. The results show that the transmittance of the TiO_2 film in the visible domain reaches 75%.Optical band gaps were calculated and found to be (3.62, 3.54, 3.45, 3.3 and 3.21) eV for the concentration of CdO x= (0.0, 0.05, 0.1, 0.15 and 0.2) wt. % respectively. At 350 nm the refractive index, extinction coefficient and dielectric constant were determined.

Keywords: $(TiO_2)_{x-1}(CdO)_x$ pulse laser deposition growth; Atomic Force Microscopy ,X-Ray diffraction .Optical properties.

الخصائص التركيبية والبصرية لأغشية اوكسيد التيتانيوم المطعمة باوكسيد الكادميوم الرقيقة المحضر بطريقة الترسيب بالليزر النبضي

الخلاصة

تم ترسيب أغشية اوكسيد التيتانيوم الرقيقة عند درجة حرارة الغرفة بتراكيز مختلفة من اوكسيد الكادميوم x= (0.0, 0.05, 0.1, 0.15,0.2) wt.% على قواعد زجاجية بتقنية الترسيب بالليزر النبضي باستخدام ليزر النديميوم ياك ذو طول موجي 1064 نانومتر وطاقة قدرها 800 ملي جول وعدد

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نبضات 500 نبضة. الخصائص التركيبة وطوبوغرافية السطح والبصرية للاغشية المرسبة أجريت باستخدام حيود الأشعة السينية، مجهر القوة الذري، مطياف الأشعة فوق البنفسجية. تم دراسة تأثير تركيز اوكسيد الكادميوم على هذه الخصائص. أثبتت نتائج حيود الأشعة السينية بان أغشية الرقيقة المرسبة هي ذات تركيب بلوري رباعي متعدد التبلور من طور Rutile مع ظهور عدة قمم عند اسطح الانعكاس (110)، (101) ، (111) و (211). كما تم دراسة الخصائص البصرية للأغشية الرقيقة بتحليل طيف النفاذية والامتصاصية وتم حساب فجوة الطاقة البصرية للاغشية المحضرة وكانت تساوي (3.62 ، 3.54 ، 3.45 ، 3.3 و 3.21) الكترون فولت بتراكيز مختلفة من اوكسيد الكادميوم x= (0.0, 0.05, 0.1, 0.15,0.2) wt.% عل التوالي. عند طول موجي 350 نانومتر تم حساب معامل الانكسار ومعامل الخمود وثابت العزل الكهربائي.

INTRODUCTION

The material of Titanium dioxide (TiO_2) is semiconductors; it is one of the group **T**ransparent **C**onducting **O**xide Semiconductors (TCOs) and high transparent in visible region and absorption in ultraviolet region, and low conductivity [1]. (TiO_2) is classified as group of (II-VI). The crystal structure for these films is tetragonal [2], and its unit cell is body center cubic (BCC), where each ion of oxygen is surrounded with two ions of titanium and with equal distance, it forms trilateral structure. Its center is an ion of oxygen, the bond which is binding between atoms of oxygen and titanium is a covalent bond results from sharing two electrons between atoms of oxygen and titanium [3]. The thin films of (TiO_2) have high band energy gap about (3.2 - 3.29) eV, (3.69- 3.78) eV for allowed and forbidden direct transition respectively [4]. Crystalline TiO_2 film exists in three phases: rutile (tetragonal with a=0.4594 nm, c=0.2958 nm), anatase (tetragonal with a=0.3785 nm, c=0.9514 nm.), and brookite (orthorhombic with a=0.9184 nm, b=0.5447 nm, c=0.5145 nm.), rutile being the most stable of the three, and the formation of its phase depending on the starting material, deposition method and temperature treatment. In particular, TiO_2 thin films can transform from amorphous phase into crystalline anatase and from anatase into rutile by changing temperature [5]. Rutile is usually the dominant phase in TiO_2 films, but in some recent work anatase-rich films have been synthesized. Cadmium oxide is also a (II-VI) of table periodic elements, n-type semiconductor with donor defects, such as Cd interstitials and oxygen vacancies. CdO thin films are prepared by many physical and chemical techniques. Various techniques such as thermal evaporation, sputtering, solution growth and pulsed laser sputtering [6, 7]. CdO has attracted attention as a transparent conducting oxides (TCOs) because of its (i) band gap (~2.5 eV), (ii) high conductivity, (iii) ease in doping, (iv) chemical stability in hydrogen plasma, (v) abundance in nature and no toxicity. **T**ransparent **C**onducting **O**xides (TCOs) have long been a subject of various investigations due to its unique physical properties and applications in commercial devices successfully used for many applications, including phototransistors, gas sensor, solar cells, liquid crystal displays, IR detectors and anti-reflection coatings [7]. CdO films have a cubic structure such as NaCl (**rock-salt)**, lattice constant equal 4.69 Å and unit cell of face center cubic (FCC) [8] as,. CdO is a promising candidate for a transparent conducting oxide material because it has a simple rock-salt crystal structure, high carrier mobility, and high conductivity, which is due to the nonstoichiometric property which resulted from oxygen vacancies in cadmium [9].

Experimental

Sample preparation

Titanium dioxide from Nano shell Company with a purity 99.99% and cadmium oxide with purity 99.99% were mixed at different concentration of x= (0.0, 0.05, 0.1, 0.15, 0.2) wt. %. The powder of precursor was mixing together using agate mortar then the mixture was pressed into pellets (1.5 cm) in diameter and (0.2 cm) thick, using hydraulic type (SPECAC), under pressure of 5 tons . finally the pellets were sintered in air at (773 K) for 3 h.

The thickness of $(TiO_2)_{1-x}(CdO)_x$ thin film was measured using an optical interferometer method employing He-Ne laser 632nm with incident angle 45°. This method depends on the interference of the laser beam reflected from thin film surface and then substrate, the films thickness t was determined using the following formula [10]:

$$t = \frac{\lambda}{2}\frac{\Delta x}{x} \qquad \dots (1)$$

Where x is fringe width, Δx is the distance between two fringes and λ is wavelength of laser He – Ne (632.8nm).

PLD and Thin Film Preparation

The $(TiO_2)_{1-x}(CdO)_x$ films were deposited on glass substrates of (2.5×7.5 cm) which are cleaned with dilated water using ultrasonic process for 15 minutes to deposit the films at room temperature by PLD technique using Nd:YAG with (λ = 1064 nm) at energy 800 mJ, repetition frequency (6Hz) for 500 laser pulse is incident on the target surface making an angle of 45° with it . The distance between the target and the laser was set to (10 cm), and between the target and the substrate was (1.5 cm), under vacuum of (3×10^{-3} mbar).

Characterization

The crystal and phase structure of $TiO_{2(1-x)}CdO_x$ thin films were examined using XRD analysis type SHIMADZU 6000 X-ray diffractometer system. The surface roughness and topography of deposited thin films was investigated using Atomic Force Microscopy (AFM) micrographs type (Digital Intruments, CSPM-AA3000). The optical properties of the films were investigated by A double –beam UV/VIS Spectrophotometer (Metertech) SP8001in the range (320-1100)nm

Results and Discussion

X-ray diffraction results

The crystalline structure of $(TiO_2)_{1-x}(CdO)_x$ recognized by study the phase of XRD for that material. Figure (1) shows the XRD patterns obtained for $(TiO_2)_{1-x}(CdO)_x$ their thin films deposited on a glass substrate with thickness equal to 200 nm by pulse laser deposition method at RT and different concentration x= (0.0, 0.05, 0.1, 0.15, 0.2) wt. %. According to American Standard for Testing Materials (ASTM) cards, the structure of thin films showed a polycrystalline tetragonal structure for TiO_2 with Rutile phase. From the Figure (1) it can be seen that the Peaks appeared at 2θ equal to 27.3 and 36 are correspond to reflection from (110) and (101) planes TiO_2 pure, also at concentration of (0.05, 0.1 and 0.15) from CdO the Peaks appeared at 2θ equal to 27.4, 36 and 54 are correspond to reflection from (110), (101) and (211) respectively ,and concentration (0.2) from CdO the Peaks appeared at 2θ equal to 27.35, 33.05 , 36 and 54.2 are correspond to reflection from (110), (111), (101) and (211) respectively, the new Peak it's from CdO.

Table (1) gives the interplaner distance d, FWHM (deg.), and grain size(nm) for the prepared samples in comparison with the standard value as in ASTM card. The structure of the $(TiO_2)_{1-x}(CdO)_x$ thin films has been investigated by using XRD to ensure the stoichiometry of our material. We can observe that the values of d and 2θ are nearly similar to that in the ASTM cards as listed in Table (1). The mean grain size of thin film calculated using the Scherer's equation [11]:

$$G = 0.94\, \lambda / \beta \cos\theta \qquad \dots (2)$$

Where G is the average crystalline grain size, λ is the wavelength, β represents the full-width at half maximum (FWHM) in radian and θ is the Bragg diffraction angle in degree. The grain sizes have been calculated by using equations (1) and tabulated in table (1).

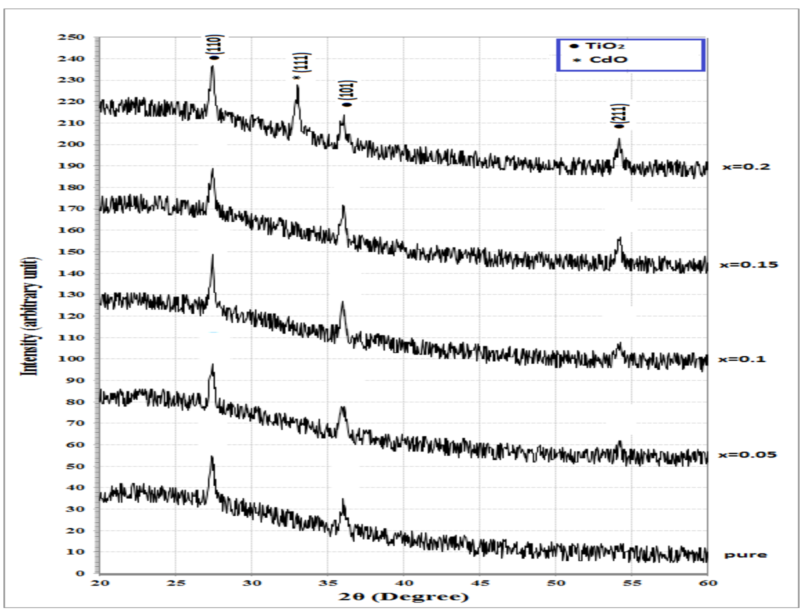

Figure (1) X-Ray diffraction pattern for $(TiO_2)_{1-x}(CdO)_x$ thin films prepared at RT and different concentration of CdO

Table (1): shows the peaks and its Bragg's angle, interplanar distance, and full width at half maximum of $(TiO_2)_{1-x}(CdO)_x$ thin films prepared at RT and different concentration of CdO

CdO %wt	2θ (Deg.)	FWHM (Deg.)	Int (Arb. Unit)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl	phase
pure	27.3	0.4542	25.50	3.264118	18	3.2548	(110)	TiO_2
	36	0.5412	21.02	2.492743	15	2.4932	(101)	TiO_2
0.05	27.4	0.4578	24.66	3.252432	18	3.2548	(110)	TiO_2
	36	0.5704	18.22	2.492743	15	2.4932	(101)	TiO_2
	54	0.6257	9.25	1.696732	14	1.6911	(211)	TiO_2
0.1	27.5	0.43202	32.23	3.240832	19	3.2548	(110)	TiO_2
	36	0.5402	22.70	2.492743	15	2.4932	(101)	TiO_2
	54.1	0.6598	13.17	1.693831	14	1.6911	(211)	TiO_2
0.15	27.4	0.4255	25.50	3.252432	19	3.2548	(110)	TiO_2
	36	0.4503	21.86	2.492743	19	2.4932	(101)	TiO_2
	54.2	0.4023	17.10	1.690942	22	1.6911	(211)	TiO_2
0.2	27.35	0.4139	26.63	3.258264	20	3.2548	(110)	TiO_2
	33.05	0.3402	27.75	2.708188	24	2.7108	(111)	CdO
	36	0.4442	10.37	2.492743	19	2.4932	(101)	TiO_2
	54.2	0.4503	17.66	1.690942	20	1.6911	(211)	TiO_2

Atomic Force Microscope (AFM):

The grain size (grain diameter) and average roughness of $(TiO_2)_{1-x}(CdO)_x$ thin films prepared at RT with different content of x= (0, 0.05, 0.1, 0.15 and 0.2)%wt are shown in Table (2). Figure (2) depicts the surface morphology of the $(TiO_2)_{1-x}(CdO)_x$ thin films analyzed by (AFM) (Scanning probe Microscope type (AA3000). From the images, it was observed that the surfaces of the films exhibited a certain degree of roughness and the film become rougher when the concentration increases. This result indicates that the growth of larger grains with increasing concentration leads to an increase in the surface roughness. It is observed that the average grain size increases with increasing of concentration and the values of the average grain size variable from (70.07 -93.17 nm) depending on film concentration as shown in table (2). This may be due to the bigger clusters formed by the coalescence of two or more grains [12]. It is clear from this Table, that there are minimum difference between the value of grain size measured by (AFM) and by (XRD) analysis. The former one measure the grain size directly which give the exact value which, the latter measure the grain size through Scherer's equation which needs some corrections. Our results are nearly in agreement with [12].

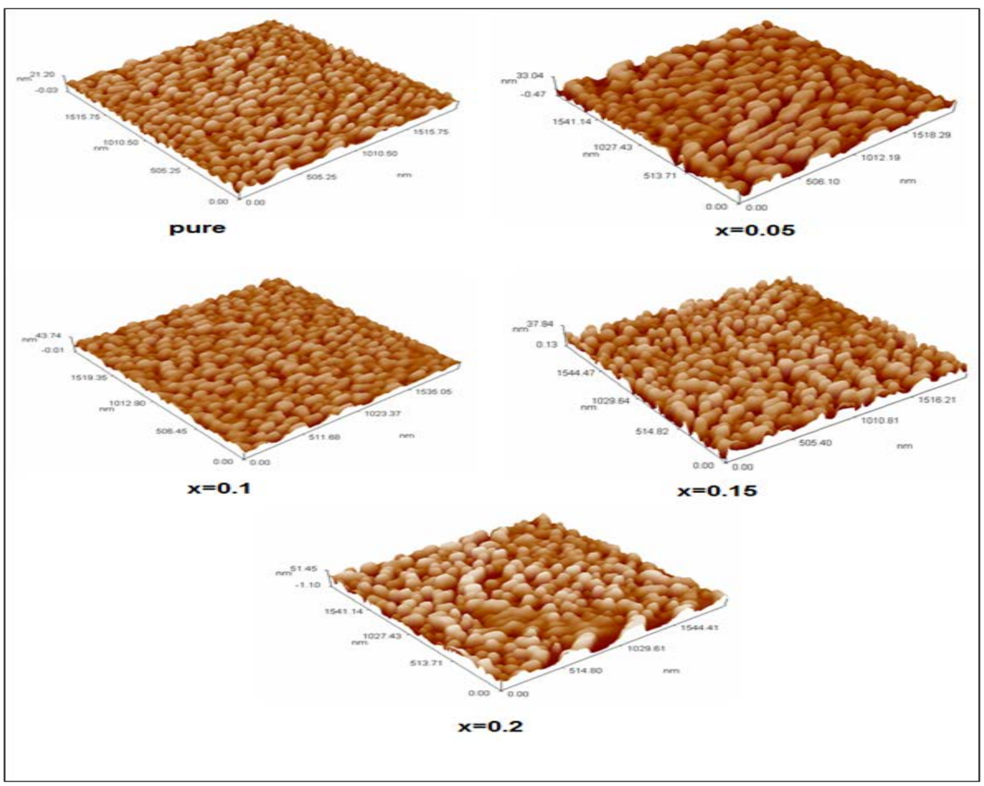

Figure (2) surface morphology of the $(TiO_2)_{1-x}(CdO)_x$ thin films analyzed by (AFM) prepared at RT at different concentrations of CdO

Table (2) shows average roughness, grain size and RMS for the $(TiO_2)_{1-x}(CdO)_x$ thin films prepared at RT and different concentration of CdO obtained from (AFM).

Content CdO %wt	Ave. grain size (nm)	Ave. Roughness (nm)	RMS (nm)
0	70.07	2.76	3.26
0.05	74.06	4.26	5.01
0.1	71.92	4.47	5.34
0.15	87.09	5.85	6.84
0.2	93.17	8.45	10

The Optical Properties of $(TiO_2)_{1-x}(CdO)_x$ Films

Transmittance spectra (T) for all films were measured and optical parameters such as, optical band gap (E_g), refractive index (n), extinction coefficient (k) were calculated. Figure (3) shows the transmittance spectra for TiO_2 at different concentration of CdO in wavelength range (320 – 1100)nm.It can be observed that the transmittance pattern of all deposited thin films increases with increasing of (λ). Also ,as shown in Figure (3) and Table (3) that the transmission values of pure TiO_2 and doped TiO_2 thin films at x= (0.0, 0.05, 0.1, 0.15 and 0.2) wt. % are 51.11 %, 33.92 %, 25.7 %, 23.04 % and 20.62 %, respectively, in the 350 nm wavelength . The increments in values of transmittance observed for pure film and decrease with increasing of concentration thin films. This deccrease in transparency is related to the structural properties of the film characteristics, because it is known that the changes in transmittance depend on the material characteristics of the films [13]. The decrease of T with the increase of CdO content attributed to that the addition of CdO to TiO_2 increases the density and consequently the samples because more opaque to the incident light.

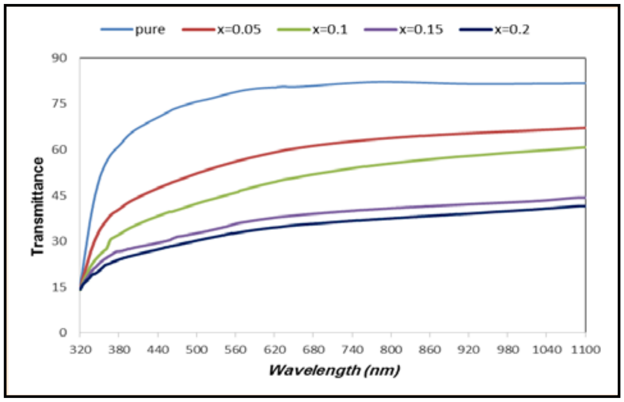

Figure (3) shows the transmittance spectra as function of wavelength at different concentration of CdO.

The absorption coefficient (α) was calculated in the fundamental absorption region from the following equation [14]:

$\alpha=2.303A/t$ … (3)

Where:

A is absorbance and t is the thickness of sample.

Figure (4) shows the variation of absorption coefficient (α) as a function of wavelength in the range of (320-1100) nm at thickness (t=200nm) for concentration of x= (0.0, 0.05, 0.1, 0.15, 0.2) wt.% prepared at RT. We can see from the figure and table (3) that (α) for $(TiO_2)_{1-x}(CdO)_x$ films increses with increasing of the concentration CdO and has high value of absorption coefficient larger than 10^4 cm^{-1} which leads to increasing the probability of occurrence direct transition between valence band and conduction band. The absorption coefficient increases rapidly at wavelength less than cut off wavelength. The reason for increase the absorption coefficient with wavelength is to generate donor levels (i.e localized states) within forbidden energy gap and conduction band.

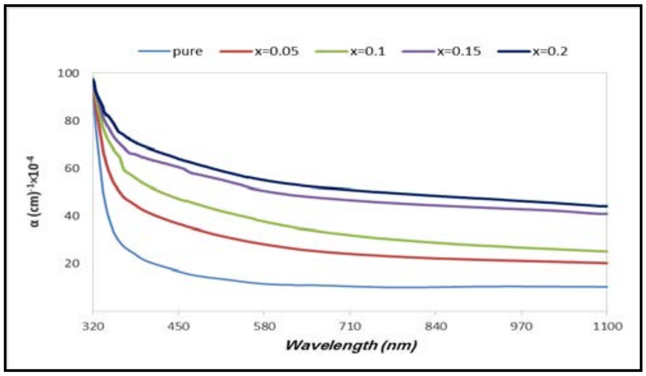

Figure (4) Absorption coefficient as a function of wavelength for $(TiO_2)_{1-x}(CdO)_x$ films at different concentration of CdO

The optical energy gap values (Eg) for $(TiO_2)_{1-x}(CdO)_x$ films have been determined by using Tauc equation [15]:

$$(\alpha h\nu) = A(h\nu - Eg)^{1/2} \qquad \dots (4)$$

Which is used to find the type of the optical transition by plotting the relations of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) and selecting the optimum linear part. The extrapolation i.e. Eg, of the portion at $(\alpha h\nu)^2 = 0$ is shown in Figure (5) The optical energy gap decreases with increasing concentration. The optical energy gap values of pure TiO_2 and CdO doped TiO_2 was (3.62, 3.54, 3.45, 3.3 and 3.21) eV for the concentration of CdO x= (0.0, 0.05, 0.1, 0.15 and 0.2) wt. % respectively. This is due to the increase of the density of localized states in the Eg ,which cause a shift to lower values**.**

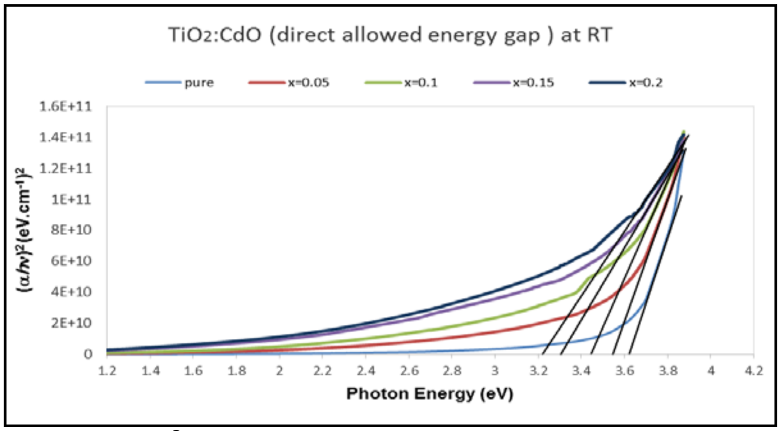

Figure (5) shows $(\alpha h\nu)^2$ as a function of hv for $(TiO_2)_{1-x}(CdO)_x$ films at different concentration of CdO

The complex optical refractive index of the films is described by the following relation [16]:

$$n^* = n - iK \qquad \dots (5)$$

Where n*: complex refractive index n is the real part and k is the imaginary part (extinction coefficient) of complex refractive index. The refractive index of the samples can be obtained from the following equation [12]:

$$n = \frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - K^2} \qquad \dots (6)$$

Where R is the reflectance and $k = (\alpha\lambda / 4\pi)$ is the extinction coefficient. The refractive index values were calculated using Eq. (6). The variation of the refractive index (n), the extinction coefficient (k) with wavelength for the TiO_2 thin films at different CdO concentrations is shown in Figs. 6 and 7 ,respectively. It can be noticed from Figure (6) and Table (3) that the refractive index decreases with the increasing concentration of CdO (2.6-1.98). The behavior of (k) can be ascribed to high absorption coefficient. And from Figure (7) and Table (3) it can see that the extinction coefficient increases with increasing the concentration of CdO (0.09-0.22).

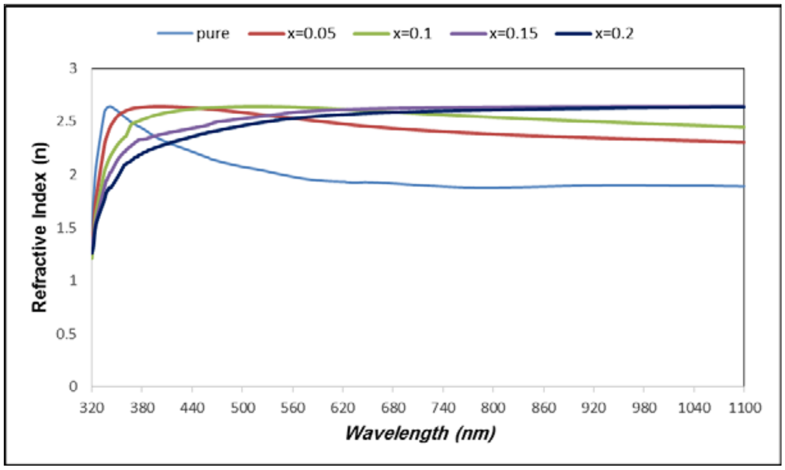

Figure (6)The variation of refractive index as a function of wavelength for $(TiO_2)_{1-x}(CdO)_x$ films at different concentration of CdO.

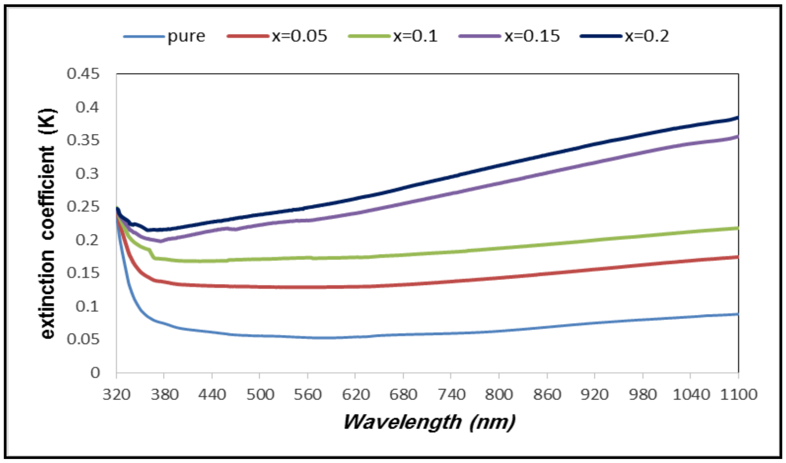

Figure (7)The variation of the extinction coefficient various wavelengths of $(TiO_2)_{1-x}(CdO)_x$ films at different concentration of CdO

Table(3): **Transmittance spectra (T) for all films, Absorption coefficient, refractive index (n), Extinction coefficient (k) and Dielectric Constant in the wavelength of 350 nm with different concentration of CdO.**

content (X)	T%	E_g(eV)	α $(cm^{-1})\times10^4$	n	k	ε_r	ε_i
0	51.11	3.62	3.36	2.60	0.09	6.75	0.49
0.05	33.92	3. 54	5.41	2.56	0.15	6.51	0.77
0.1	25.70	3.45	6.79	2.29	0.19	5.19	0.87
0.15	23.04	3.3	7.34	2.14	0.21	4.55	0.88
0.2	20.62	3.21	7.89	1.98	0.22	3.87	0.87

Dielectric Constant Measurements:

Both real (ε_r) and imaginary (ε_i) dielectric constant are measured for prepared films by using from the following equation [17]:

The real part of dielectric constant

$$\varepsilon_r = n^2 - k^2 \quad \dots (7)$$

The imaginary part of dielectric constant

$$\varepsilon_i = 2nK \quad \dots (8)$$

Figures (8) and (9) illustrate variation of (ε_r) and (ε_i) as a function of wavelength. It is observed that from the table the real part of dielectric constant decreases and the imaginary part increases with increasing concentration this is due to the decrease of the refractive index and increases the extinction coefficient with wavelength.

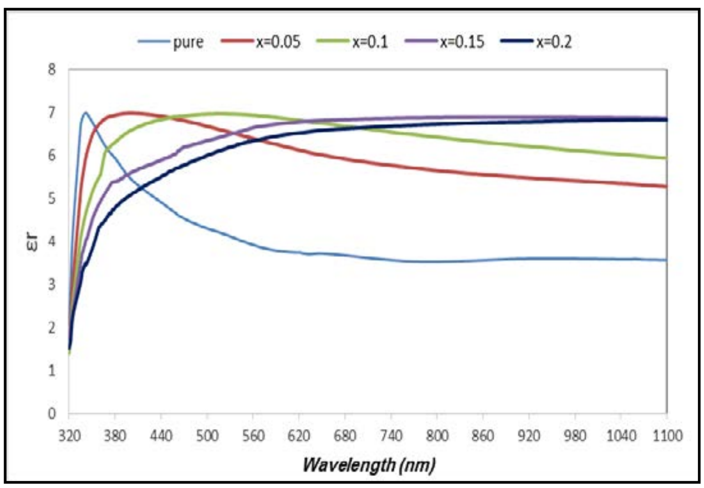

Figure (8)The Variation of the Real Part of Dielectric Constant (ε_r) With Wavelength of $(TiO_2)_{1-x}(CdO)_x$ films at different concentration of CdO

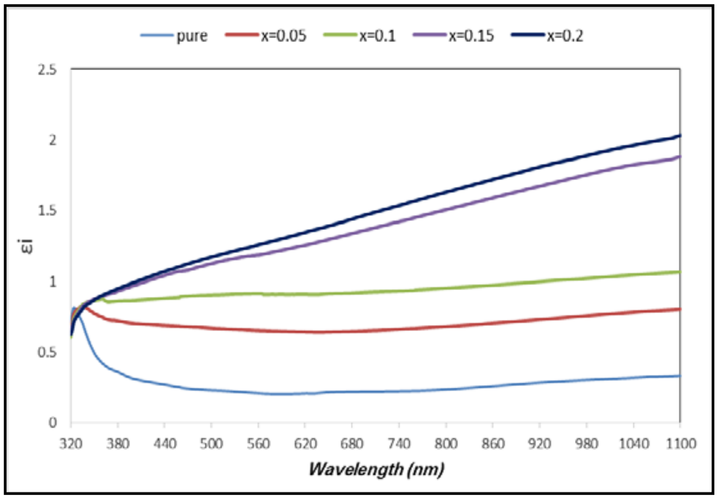

Figure (9)The Variation of the imaginary Part of Dielectric Constant (εi) with Wavelength of $(TiO_2)_{1-x}(CdO)_x$ films at different concentration of CdO

Conclusion

In this paper the structural, morphological, and optical properties of TiO_2 films which are deposited using the PLD technique were investigated. By structural and optical properties of the films were analysed by means of XRD, AFM, and UV–Vis-NIR spectrophotometry. The XRD characterization shows a polycrystalline films with rutile phase. The AFM investigations show no cracks in the film and a larger grains with increasing concentration of CdO leads to an increase in the surface roughness. It is observed that the average grain size increases with increasing of concentration. As well as the refractive index, *n*, and the extinction coefficient, *k*, in the 200 to 800 nm wavelength range. In addition, we found that the transmittance the TiO_2 film in the visible domain reaches 75% in a large spectral range.

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