Structural and photoluminescence 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 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 technique (PLD) using Nd-YAG laser with λ=1064nm, energy=800mJ and number of shots=500. The thickness of the film was 200nm. The films were annealed to different annealing (423 and 523) k. The effect of annealing temperatures and concentration of CdO on the structural and photoluminescence (PL) properties were investigated. X-ray diffraction (XRD) results reveals that the deposited $TiO_{2(1-x)}CdO_x$ thin films were polycrystalline with tetragonal structure and many peaks were appeared at (110), (101), (111) and (211) planes with preferred orientation along 2Ө around 27.3^0. The results of photoluminescence (PL) emission show that there are two peaks positioned are around 320 nm and 400 nm for predominated peak and 620 nm and 680 nm for the small peaks.

Key words

TiO_2:CdO Thin Film, structural properties, photoluminescence (PL) properties pulse laser deposition technique.

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الخصائص التركيبية والاستضائية لاغشية اوكسيد التيتانيوم المطعمة باوكسيد الكادميوم المحضرة بواسطة الترسيب بالليزر النبضي

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الخلاصة

تم ترسيب اغشية أوكسيد التيتانيوم الرقيقة المطعمة بأوكسيد الكادميوم بنسب وزنية مختلفة من اوكسيد الكادميوم (x= 0.0, 0.05, 0.1, 0.15 ,0.2) على ارضيات زجاجية بواسطة تقنية الترسيب بالليزر النبضي باستخدام ليزر النديميوم – ياك ذي الطول الموجي 1064 نانومتر وطاقة مقدارها 800 ملي جول وعدد ضربات 500 وكان سمك الغشاء الرقيق 200 نانومتر، كما تم تلدين الاغشية حرارياً في درجات تلدين مختلفة (423، 523) كلفن. تم دراسة تأثير التلدين ونسبة التطعيم بأوكسيد الكادميوم على الخواص التركيبية والاستضائية للاغشية ، بينت نتائج فحوصات الاشعة السينية ان الاغشية المرسب متعددةالبلورات تركيب سداسي مع ظهور عدة قمم تظهر عند اسطح الانعكاس (111), (101), (110) و (211) حيث كان افضل اتجاه على طول الزاوية 27.3 درجة. أظهرت نتائج انبعاث الاستضائية ان هنالك قمتين مابين الطول الموجي 320 نانومتر الى 400 نانومتر للقمة العظمى ومابين 620 نانومتر الى 680 نانومتر للقمة الصغرى.

Introduction

Titanium dioxide has been one of the most extensively studied oxides because of its remarkable optical and electronic properties [1–3]. TiO_2 films have attracted attention for use in fabricating capacitors in microelectronics devices due to their unusually high dielectric constant [4,5]. 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 [6]. Crystalline TiO_2 film exist 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 [7,8]. Rutile is usually the dominant phase in TiO_2 films, but in some recent work anatase-rich films have been synthesized. Many deposition methods can be used to prepare titanium oxides film: thermal [9] or anodic [10] oxidation of titanium, electron beam evaporation [11], chemical vapor deposition [12], plasma-enhanced chemical vapor deposition [13], sol–gel method [14, 15] and reactive sputtering methods [16–19] Recently there are many applications of laser one of these applications in a thin film preparation field that called pulsed Laser deposition (PLD). With the pulsed laser deposition method, thin films are prepared by the ablation of one or more targets illuminated by a focused pulsed-laser beam. This technique was first used by smith and Turner in 1965 [20] for the preparation of semiconductor and dielectric thin films and was established due to the work of Dijkkamp and coworkers [21] on high-temperature superconductors in 1987. Cadmium oxide (CdO) has high electrical conductivity and high optical transmittance with a moderate refractive index in the visible region of the solar spectrum. In recent years it has found various applications in transparent electrodes, solar cells, photo transistors, photodiodes, gas sensors, etc. [22, 23]. CdO films are wide, direct band-gap semiconductors with an optical energy gap of about 2.4 eV at room temperature. CdO, with its cubic structure, is also a II-VI n-type semiconductor with donor defects, such as Cd interstitials and oxygen vacancies [24].

Experimental details

1. 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 cadmium oxide of (x= 0.0, 0.05, 0.1, 0.15, 0.2) Wt. %. The powder of precursor was mixed together using agate mortar, the mixture was then pressed into pellets (1.5 cm) in diameter and (0.2 cm) thick, using hydraulic type (SPECAC), under pressure of 5 tons. The pellets were sintered in air at temperature (773 K) for 3 h.

2. Thin films preparation of $TiO_{2(1-x)}CdO_x$ by PLD

$TiO_{2(1-x)}CdO_x$ films were deposited on glass slides substrates of (10×10 mm) at room temperature and different concentration of CdO. The glass substrate was cleaned with dilated water using ultrasonic process for 15 minute to deposit the films at room temperature then annealing treatment at (423 and 523) K by furan (Precision Model 19 Vacuum Oven made in west Germany) under vacuum ($8*10^{-2}$ mbar). Finally, deposited thin films from TiO_2:CdO by PLD technique using Nd:YAG with (λ= 1064 nm) SHG Q-switching laser beam at 800 mJ, repetition frequency (6Hz) for 500 laser pulse is incident on the target surface making an angle of 45° with it as shown in Fig. 1.

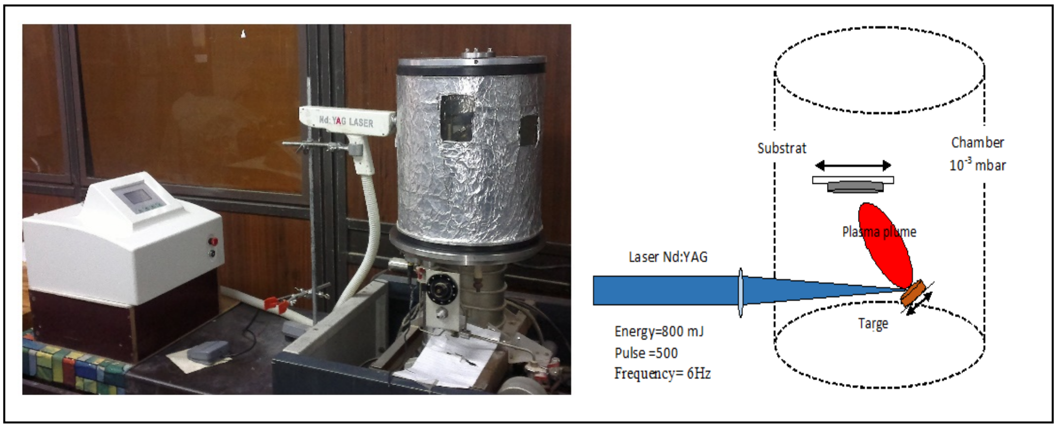

Fig.1: PLD set up using Nd:YAG with λ= (1064 nm).

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 (10^{-3} mbar). The thickness of $TiO_{2(1-x)}CdO_x$ thin film was measured using an optical interferometer method employing He-Ne laser 0.632 μm 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 [25]:

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

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

3. Characterization

XRD analysis using SHIMADZU 6000 X-ray diffractometer system was employed in order to obtained the crystal quality and phase structure of the films. The optical properties of $TiO_{2(1-x)}CdO_x$ thin films were investigated by PL spectroscopy using UV light excitation SL-174 (ELICO) Spectro Fluorometer, 150 watt Xenon Arc lamp, (EX and Em) from (200-900) nm, at photo excitation 350nm.

Results and discussion

1. Structural properties

The crystalline structure for $TiO_{2(1-x)}$ CdO_x recognized by study the phase of XRD for that material. Figs. (1-a, b, c) show the XRD patterns obtained for $TiO_{2(1-x)}CdO_x$ thin films deposited on glass substrate with thickness of 200 nm by pulse laser deposition method at different concentration of CdO x= (0.0, 0.05, 0.1, 0.15, 0.2) Wt. % prepare at RT and annealed to different annealing temperatures (423 and 523) K, respectively. According to American Standard for Testing Materials (ASTM) cards, the structure of thin films showed a polycrystalline tetragonal structure for TiO_2 of Phase classification Rutile. From Fig. 2 it can be observed that the preferred orientation was along (110) direction for Rutile. In the x-ray patterns, it is cleared that the peaks intensities increase with increasing of the doping ratio from 5 to 20%. Also, it was noticed that the all film quality improves with the increasing of annealing temperature, and appear a new peak at concentration (0.15 and 0.2) Wt. % which recognized to CdO structure that corresponding to the reflection plane of (111).

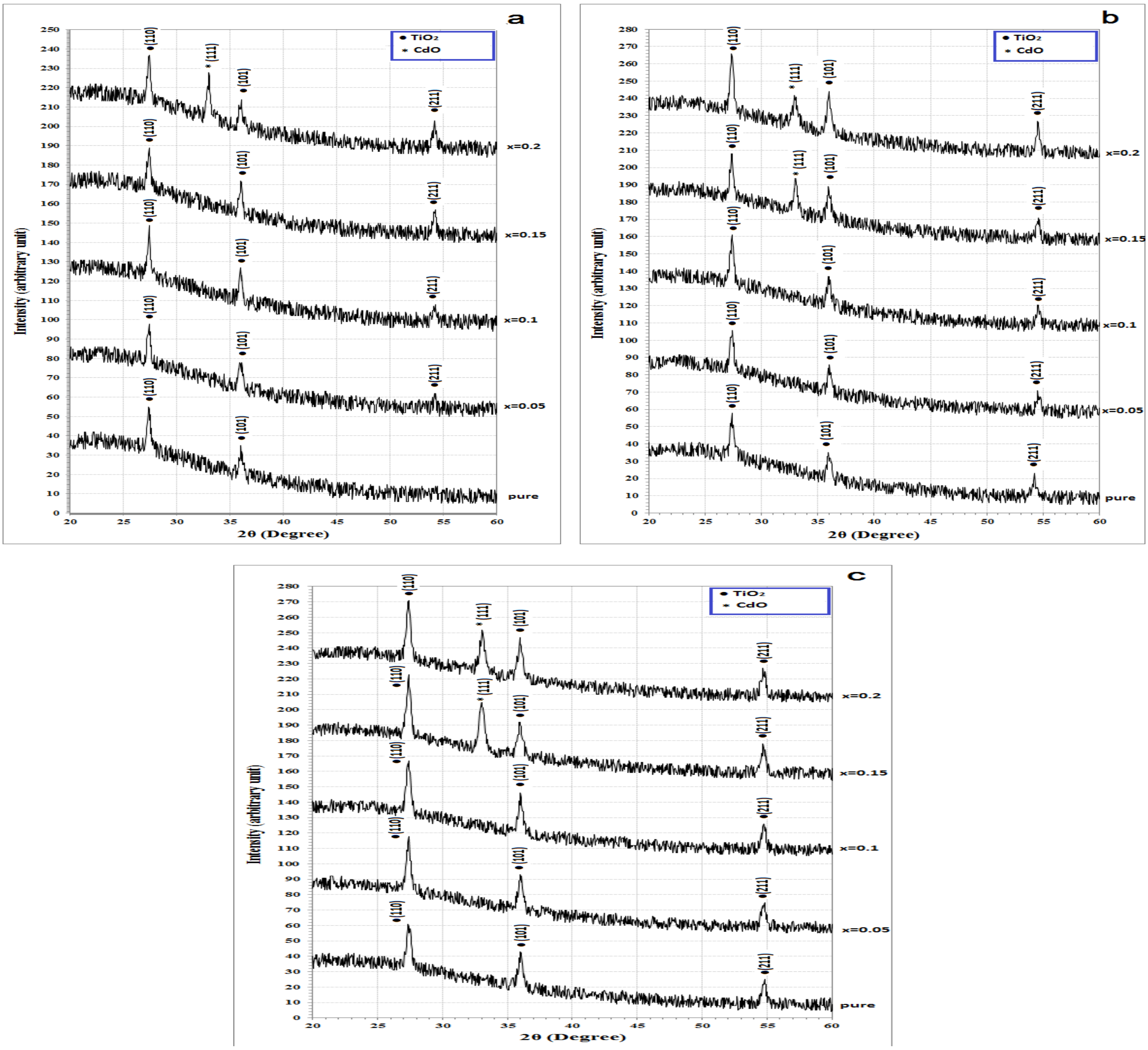

Fig. 2: The X-Ray diffraction for TiO_2: CdO thin films: a) at RT, b) at annealing 423K, c) at annealing 523K.

Table (1-a, b, c) gives the interplaner distance d, FWHM (Deg.), and grain size for the prepared samples in comparison with the standard value as in ASTM card. The structure of the TiO_2: CdO film 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 [26]:

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

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 Eqs. (1) and tabulated in Table 1. It is cleared from the table that d_{hkl} and grain size increases with increasing of concentration of x. This implies that Cd partially substituted for Ti in TiO_2 structure.

Table 1: The peaks and its Bragg's angle, interplanar distance, and full width half at maximum for TiO_2: CdO thin films at different annealing temperatures and different concentration of CdO.

Ts (K)	Content.	2θ (Deg.)	FWHM (Deg.)	Int (Arb. Unit)	d_{hkl} Exp.(Å)	G.S (nm)	d_{hkl} Std.(Å)	hkl
RT	pure	27.3	0.4542	25.50	3.2641	18	3.2548	(110)
		36	0.5412	21.02	2.4927	15	2.4932	(101)
	0.05	27.4	0.4578	24.66	3.2524	18	3.2548	(110)
		36	0.6704	18.22	2.4927	12	2.4932	(101)
		54	0.45421	9.25	1.6967	20	1.6911	(211)
	0.1	27.5	0.43202	32.23	3.2408	19	3.2548	(110)
		36	0.6402	22.70	2.4927	13	2.4932	(101)
		54.1	0.6598	13.17	1.6938	14	1.6911	(211)
	0.15	27.4	0.4255	25.50	3.2524	19	3.2548	(110)
		36	0.4503	21.86	2.4927	19	2.4932	(101)
		54.2	0.4023	17.10	1.6909	22	1.6911	(211)
	0.2	27.35	0.4139	26.63	3.2582	20	3.2548	(110)
		33.05	0.3402	27.75	2.7081	24	2.7108	(111)
		36	0.4442	10.37	2.4927	19	2.4932	(101)
		54.2	0.4503	17.66	1.6909	20	1.6911	(211)
423	pure	27.5	0.3916	26.68	3.2408	21	3.2548	(110)
		36	0.4633	17.42	2.4927	18	2.4932	(101)
		55.1	0.4212	16.10	1.6654	21	1.6911	(211)
	0.05	27.3	0.3756	26.68	3.2641	22	3.2548	(110)
		36	0.4791	20.95	2.4927	17	2.4932	(101)
		55.2	0.4949	13.67	1.6627	18	1.6911	(211)
	0.1	27.15	0.3554	28.01	3.2818	23	3.2548	(110)
		36.05	0.3791	24.26	2.4894	22	2.4932	(101)
		55.2	0.4212	11.47	1.6627	21	1.6911	(211)
	0.15	27.05	0.3521	29.77	3.2937	23	3.2548	(110)
		33.05	0.3370	13.23	2.7082	25	2.7108	(111)
		36	0.3347	22.27	2.4927	25	2.4932	(101)
		55.4	0.4476	12.35	1.6571	20	1.6911	(211)
	0.2	27.1	0.3389	31.09	3.2878	24	3.2548	(110)
		33.05	0.2994	16.32	2.7082	28	2.7108	(111)
		36.05	0.2949	18.74	2.4894	28	2.4932	(101)
		55.6	0.4476	14.55	1.6516	20	1.6911	(211)
523	pure	27.5	0.3654	27.73	3.2408	22	3.2548	(110)
		36.5	0.4310	18.37	2.4597	19	2.4932	(101)
		55.25	0.4867	13.50	1.6613	18	1.6911	(211)
	0.05	27.5	0.3547	28.81	3.2408	23	3.2548	(110)
		36	0.3097	24.67	2.4927	27	2.4932	(101)
		55.25	0.3540	11.70	1.6613	25	1.6911	(211)
	0.1	26.75	0.3441	30.79	3.3300	24	3.2548	(110)
		35.9	0.2655	21.61	2.4995	31	2.4932	(101)
		54.65	0.3655	15.48	1.6781	24	1.6911	(211)
	0.15	27.65	0.3115	30.97	3.2235	26	3.2548	(110)
		33	0.2867	12.60	2.7121	29	2.7108	(111)
		35.85	0.2982	19.63	2.5028	28	2.4932	(101)
		54.3	0.4248	14.40	1.6880	21	1.6911	(211)
	0.2	27.65	0.2954	33.31	3.2235	28	3.2548	(110)
		33.1	0.2212	17.47	2.7042	37	2.7108	(111)
		35.25	0.2097	26.11	2.5440	40	2.4932	(101)
		54.25	0.4425	14.04	1.6892	20	1.6911	(211)

2. **Photoluminescence (PL)**

Photoluminescence (PL) of the deposited $TiO_{2(1-x)}CdO_x$ films on glass substrate at Room temperature and treated at different annealing temperatures (T = 423 and 523) K for one hour under vacuum with pressure (10^{-3}mbr) and different concentration of CdO at x= (0.0, 0.05, 0.1, 0.15, 0.2) wt.% were measured.Fig. (3-a, b, c) shows the PL spectrum of the $TiO_{2(1-x)}CdO_x$ films at room temperature and annealed to different annealing temperatures and different concentration of CdO. Typical luminescence behavior with two emission peaks, UV PL characteristics of $TiO_{2(1-x)}CdO_x$ films showed strong relation to the temperature. The first peak in PL spectra between (320-400) nm corresponds to the direct recombination between electrons in the conduction band and holes in the valence band [27]. In all the samples (pure and dopant) a broad peak was also observed at a lower energy or visible region (second peak). The intensity of the two peaks increases markedly with the increase of concentration, due to the large exciton bending energy of $TiO_{2(1-x)}CdO_x$. Higher energy (shorter wavelength) excitation photons cause more phonons to be emitted before luminescence occurs. If the excitation energy is less than the energy difference between the ground state and the first excited state, then no optical absorption will occur, resulting in no PL. The PL emission might have close relation with the luminescence of the recombination of photo induced electrons and holes, the free and self- trapped electron-hole pair or excitons, which possibly resulted from the nointegrality of nano-sized TiO_2 crystallite such as the lattice distortion and surface oxygen deficiencies. However, in thin films, the broad band visible emission at (620-680) (nm) this luminescence could be due to the self-trapped excitons of the charge transfer process. The Table 2 shows the peak values and the energy of the luminescence spectrum of all samples. It is observed from this table The value of the optical energy gap increases with increasing of Ta for all samples, this is due to the growth of grain size and the decrease in defect states near the bands and these in turn increase the value of E_g. The optical energy gap decreases with increasing concentration this is due to the increase of the density of localized states in the E_g which cause a shift to lower values.

Conclusion

Pure TiO_2 and $TiO_{2(1-x)}CdO_x$ thin films were deposited by PLD technique on glass substrates with different concentration of CdO at RT and annealed to different annealing temperatures (423 and 523) K. The resulting of $TiO_{2(1-x)}CdO_x$ films were characterized by XRD measurement and PL properties. X-ray diffraction (XRD) results reveals that the deposited $TiO_{2(1-x)}CdO_x$ thin films were polycrystalline with tetragonal structure of Phase classification Rutile Annealing the films in vacuum for one hour increases the grain size and noticed that the all film quality was improved and appear a new peak at content of (0.15 and 0.2) Wt. % which recognized to CdO structure. From PL analysis it is observed two emission peaks, UV PL characteristics of for pure TiO_2 and doped TiO_2 with CdO and the intensity gradually increases by increasing the doping.

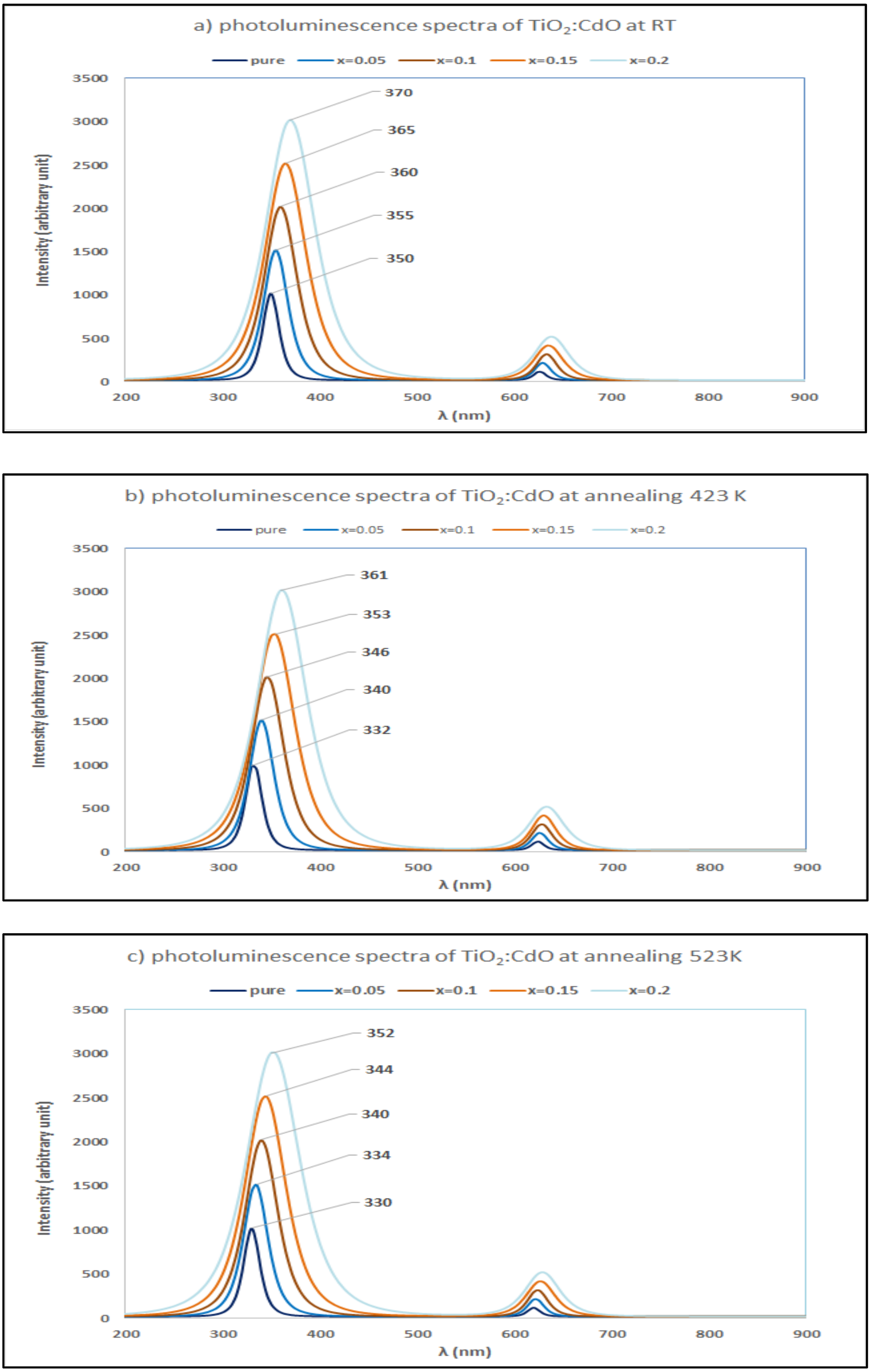

Fig. 3: Photoluminescence spectra for TiO_2: CdO thin films: a) at RT, b) at annealing 423K, c) at annealing 523K.

Table 2: The peak values and the energy of the luminescence spectrum of all samples.

Ts (K)	content x	wavelength (nm)	E_g (ev)	wavelength (nm)	E_g (ev)
		first peak		second peak	
RT	0	350	3.543	627	1.978
	0.05	355	3.493	630	1.968
	0.1	360	3.444	634	1.956
	0.15	365	3.397	636	1.950
	0.2	370	3.351	639	1.941
423	0	332	3.735	624	1.987
	0.05	340	3.647	626	1.981
	0.1	346	3.584	628	1.975
	0.15	353	3.513	630	1.968
	0.2	361	3.435	633	1.959
523	0	330	3.758	620	2.000
	0.05	334	3.713	622	1.994
	0.1	340	3.647	624	1.987
	0.15	344	3.605	627	1.978
	0.2	352	3.523	629	1.971

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