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Influence of Substrate Temperature on Structure and Optical Properties of CdO Thin Films Prepared By Pulsed Laser Deposition

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ABSTRACT

Nanocrystallites of cadmium oxide (CdO) thin films were deposited by pulsed laser deposition technique on glass substrates using Nd:YAG laser at 532nm wave length. X-ray diffraction (XRD) patterns confirmed the nanocrystalline cubic CdO phase formation. The intensity of XRD peaks increases with the increase in substrate temperature and better crystallinity takes place at higher temperature. The morphology of deposited films were characterized by scanning electron microscope (SEM) and atomic force microscope (AFM); with increasing substrate temperature, both the grain size and surface roughness increase .The grain size value (12,18,47 nm) and rms roughness values were 63.3, 98.8 and 138.4 nm for thin films deposited at 100 , 200 and 300°C respectively. UV–Vis spectrophotometric measurement showed high transparency (nearly 88 % in the wavelength range 500–900 nm) of the CdO thin film with a direct allowed band gap value lying in the range 2.81–3.7eV.

Keywords: Nanostructure Cadmium oxide, Transparent conducting oxides, PLD.

تأثير درجة حرارة القاعدة على الخصائص التركيبية والبصرية لأغشية أوكسيد الكادميوم المحضرة بطريقة الترسيب بالليزر النبضي

الخلاصة

في هذا البحث تم تحضير اغشية رقيقة نانوية من اوكسيد الكادميوم (CdO) بطريقة الترسيب بالليزر النبضي على قواعد من (الزجاج) باستخدام ليزر الأنديك النبضي ذو الطول الموجي 532 نانومتر. حدد التركيب البلوري باستخدام حيود الأشعة السينية (XRD) اذ أظهرت النتائج تكون الطور المكعب لأغشية اوكسيد الكادميوم البلورية. ازدادت شدة قمم حيود الاشعة السينية بزيادة درجة حرارة القاعدة بمعنى ازدياد تبلور الغشاء عند درجات الحرارة العالية . حددت خصائص طبوغرافية السطح من خلال قياس المجهر الالكتروني الماسح و مجهر القوى الذرية , حيث بزيادة درجة حرارة القاعدة ازداد كل من الحجم الحبيبي وخشونة السطح . بلغت قيمة الحجم الحبيبي (12,18,47) نانومتر وقيمة خشونة السطح 138.4 , 98.8 ,63.3 نانومتر للأغشية المحضرة بدرجات حرارة قاعدة (100,200,300) °C على التوالي. اظهرت نتائج قياسات مطياف الاشعة المرئية والفوق البنفسجية امتلاك غشاء اوكسيد الكادميوم نفاذية عالية تصل تقريبا" إلى 88 % عند مدى الطول الموجي(900-500) نانومتر مع قيمة فجوة طاقة الانتقال المباشر المسموح تقع عند المدى (2.81-3.7) الكترون فولت.

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INTRODUCTION

Due to the nature of their excellent electrical conductivity and optical transmission, transparent conductive oxides (TCOs) have been used in many applications, such as windows of wavelength for solar cell , flat panel displays, photovoltaic devices, smart windows, and deicing heaters on vehicles. The TCOs used in solar cells should be highly transparent to the solar spectrum, have low electrical resistivity [1], be stable under high vacuum plasma, and have a suitable structure in particular for a-Si solar cells. For other applications additional criteria can be of importance, which include physical, chemical, and thermal durability, etchability, work function, uniformity, toxicity, and cost [2]. Although CdO was the very first reported transparent conducting film made by oxidation of sputtered metallic cadmium [3], it has not been extensively studied compared to other TCOs due to its relatively small bandgap. A variety of thin film deposition techniques, like spray pyrolysis [4, 5 and 6], ion beam sputtering [6], chemical bath deposition [7], activated reactive evaporation [8], thermal oxidation [9], reactive sputtering [10 and 11], and sol–gel [12] have been employed to produce CdO films. CdO is an n-type semiconductor with a NaCl structure, transparent in the visible region with a direct band gap of 2.5 eV. Nonstoichiometric undoped CdO thin films usually exhibit low resistivity due to native defects of oxygen vacancies and cadmium interstitials. Hence, low-resistivity films can be obtained by controlling these native defects. no CdO films have been made meeting both the high conductivity and transmittance requirements for solar cell applications [13]. In this paper, we report the successful growth of pure CdO thin films on glass substrates by pulsed laser deposition technique. We study the structure and optical properties as a function of substrate temperature.

EXPERIMENTAL PROCEDURE

Film Preparation

The deposition was carried out using a Q switched Nd:YAG laser with a frequency second radiation at 532nm (pulse width 7ns repetition rate 10HZ) and fluencies energy 1.2 J/cm^2 . The studied films were prepared from pure CdO targets and grown by pulsed laser deposition on an optically Flat glass substrates kept an on-axis distance of 4cm from the CdO target. The chamber was kept at vacuum pressure of 10^{-5} mbar as shown in Fig.(1). The CdO disc was ablated from 10-100 pulses (10-20 min) to get single layered thin films. Consequently, During the deposition the substrate temperatures (Ts) were kept at 100, 200 and 300 $^{\circ}$C respectively . In fixed O_2 pressure 10^{-2} Torr. The deposited film had a thickness of approximately 150 nm. The thickness of the film was estimated from cross-sectional scanning electron microscopy (SEM_JEOL 7000) measurement.

Film Characterization

The crystalline structure of the films was determined by XRD measurements (Philips PW 1050, λ=1.54 A^0). The surface morphology was examined by scanning electron microscopy (SEM–JEOL 7000) and by atomic force microscopy (AFM-Digital Instruments NanoScope) working in tapping mode. Optical Transmission spectra of all the films were recorded using a UV-ViS (Perkin Elemer Company) spectrophotometer, in the spectral range of (300-900)nm.

RESULTs AND DISCUSSION

X-ray diffraction patterns of the CdO thin films has been shown in Fig (2) for different substrate temperatures (a) 100°C, (b) 200°C, and (c) 300°C. The several peaks of cubic face-centered CdO with $a_\circ$ = 4.6953 A° have been obtained due to diffraction form (1 1 1), (2 0 0), (2 2 0) and (3 1 1) planes.

The information on strain (ε) and the particle size (L) of the deposited films have been obtained from the following relation [5]:

$$\beta \cos \Theta/\lambda = 1/L + \varepsilon \sin\Theta/\lambda \qquad \ldots.(1)$$

where β is the full widths at half maximum (FWHM) of the diffraction peaks.

Figure (3) represents the plot of β cosΘ/λ vs. sin Θ/λ. Slope of the graph depicts the strain values which lie in the range 0.031–0.036 and the intercept on y-axis gives the crystallite size which lie in the range 2.4– 15.4 nm.

Figure 4 shows the variation of grain size and strain with substrate temperatures. It is clear from the figure that as the substrate temperatures increases, the grain size also increases but the strain value decreases.

Figure (5) shows the SEM images of the CdO thin films deposited at substrate temperatures of 100, 200 and 300°C, respectively. CdO thin films have a quite uniform and hole-free surface. At 100,200 and 300 °C the film has homogeneous surface morphology, with a wide size distribution of the particles about 10,18,44 nm . With increasing substrate temperature, the average size of aggregated particles increases. When the substrate temperature reaches 300 °C, the particle size increases obviously. The average grain size deduced from x-ray diffraction using the Scherrer's formula is estimated at ~ (12- 47) nm. From XRD data the grain size larger than that estimated from SEM micrograph (see Table 1).The cross-section SEM image indicates that the prepared CdO film also exhibits a roughness surface structure and its thickness is about 150 nm.

Figure (6) shows the AFM images of the CdO thin films deposited at substrate temperatures of 100 , 200 and 300°C. The surface morphology of the CdO thin films as observed from the AFM micrographs proves that the grains are uniformly distributed within the scanning area (10 µm x 10 µm), with individual columnar grains extending upwards.

From the topographic images it can be seen that the films deposited at 100 °C appears to be more uniform than the topography of the sample deposited at 200 and 300°C. The RMS roughness also increased with increasing substrate temperatures

(T_s), the section analysis shows that RMS roughness values are 63.31, 98.84 and 138.35 nm for thin films deposited at 100 , 200 and 300 °C respectively. Substrate temperature certainly changes the topography drastically as shown in Table (1) . A possible explanation for this observation is that surface mobility of the adatoms is higher at higher temperature (300 °C) ,this results in higher surface diffusion length, island separation, and lateral size. When island separation length is greater than the lateral size of the island, terrace and stairs topography are normally favored . On the other hand, surface mobility of the adatoms are lower at lower temperature (100 °C), thus islands are more closely spaced. If island separation is smaller than the island lateral size, more uniform growth of the thin film is preferred(see Table 1).

Figure (7) shows the transmittance versus wavelength traces which show nearly 87 % transmittance in the wavelength range of 500–900 nm. The fundamental absorption, which corresponds to electron excitation from the valance band to conduction band, can be used to determine the nature and value of the optical band gap. For all the films analyzed it is observed that the optical transmittance decreases slightly with increasing the substrate temperature This is in consistent with the increase of the surface roughness promoting the increase of the surface scattering of the light. Both densification and agglomeration of the crystallites at the highest temperature are responsible for this behavior according to the results obtained by [5,12].

The relation between the absorption coefficients (α) and the incident photon energy (hν) can be written as [8],

$$(\alpha h\nu)^{1/n} = A(h\nu - Eg) \qquad \ldots.(2)$$

where A is a constant and Eg is the band gap of the material and exponent n depends on the type of transition. For direct allowed n = 1/2, indirect allowed transition, n = 2, and for direct forbidden, n = 3/2. To determine the possible transitions, $(\alpha h\nu)^{1/n}$ versus hν were plotted and corresponding band gap were obtained from extrapolating the straight portion of the graph on hν axis. The direct band gap calculated from $(\alpha h\nu)^2$ versus hν plots (as shown in Figure 8.a) lie in the range 2.81–3.7eV and indirect band gap calculated from $(\alpha h\nu)^{1/2}$ versus hν plots lie in the range 2–2.42 eV (as shown in Figure 8.b) .Substrate temperature having different effect leads to increase in the optical energy gap values, because the increasing substrate temperature process decreases from the secondary levels and the structure defects which lead to the contract tails region. Both the direct band gap and indirect band gap values of the films are higher than that of the value of bulk materials because of quantum confinement of CdO nanocrystals [7] (see Table 1).

CONCLUSIONS

In conclusion, nanostructured deposits of CdO were prepared in vacuum and under 10^{-2} Torr of oxygen on glass substrates by nanosecond PLD at 532 nm. The effects of substrate temperature on the crystal structure were discussed and analyzed. X-ray diffraction studies revealed that the films were polycrystalline and cubic CdO phase

formation. The XRD peaks are more broaden at lower temperature which indicate that the quantum confinement is better at lower temperature.The surface morphology of the deposits materials have been studied by using scanning electron (SEM) and atomic force microscopes (AFM). The grain size of the nanoparticles observed at the surface depended on the substrate temperature. Optical transmission spectrum showed nearly 88% transmittance in the wavelength range of 500–900 nm and high direct bandgap lies in the range 2.81–3.7 eV. The indirect bandgap of the films (lies in the range 2–2.42 eV) are also higher than that of the bulk CdO materials. This may be due to quantum confinement effect of CdO nanoparticles.

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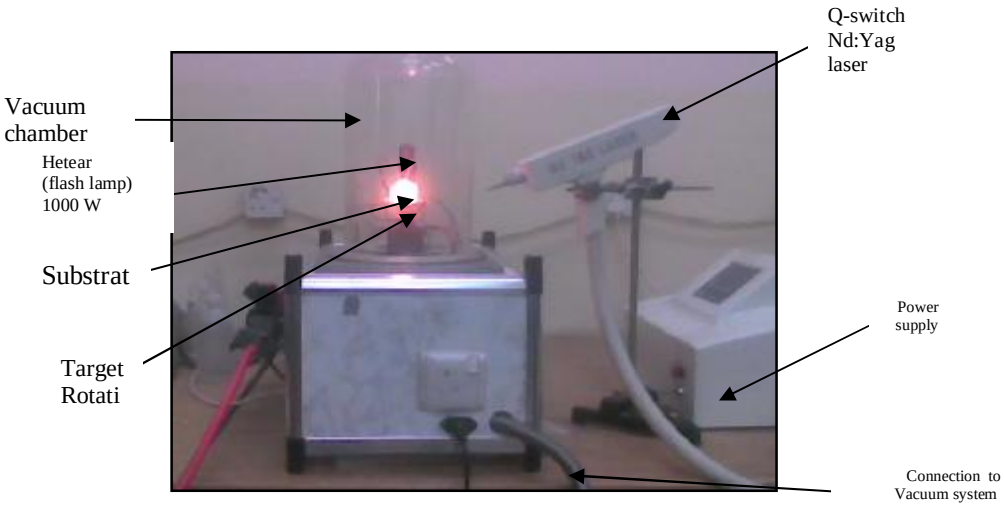


Figure (1) Experimental setup

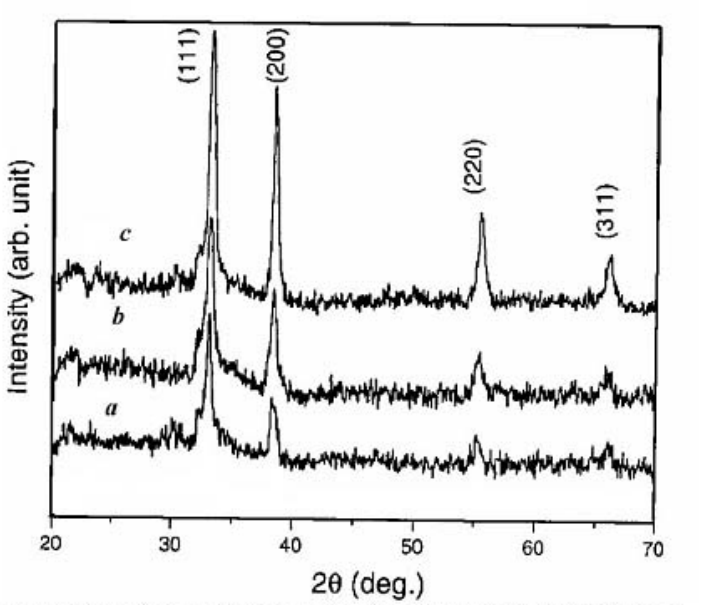
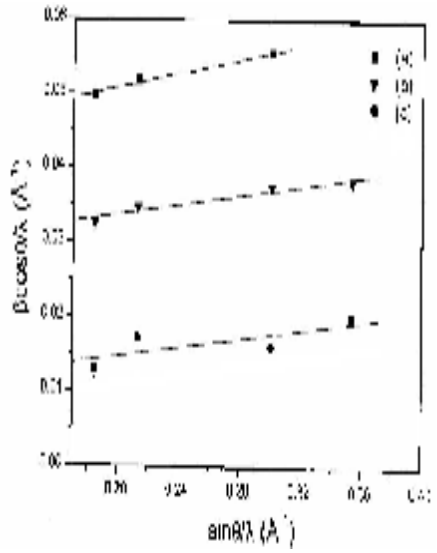


Figure 2. XRD patterns of a nanocrystalline CdO thin films deposited on $_{glass}$ substrates at different substrate temperature (a) 100°C, (b) 200°C and (c) 300°C .



Figure(3) Plot to determine the particle size and strain of nanocrystalline CdO thin films for different substrate

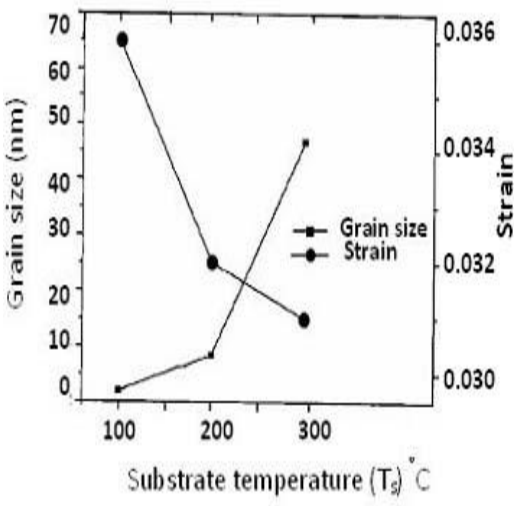
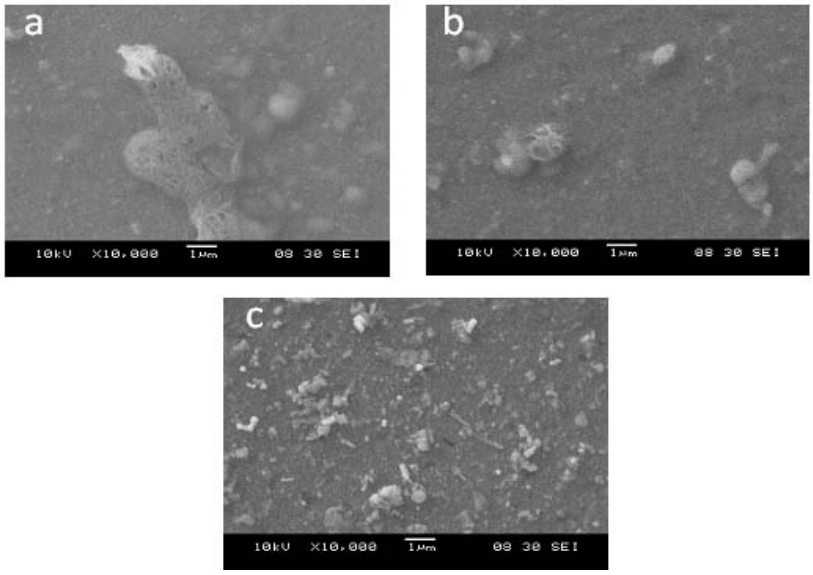


Figure (4) Variation of crystallite size and strain with substrate temperature.



Figure(5) SEM image of CdO film grown at different substrate temperatures on glassa) 100 °C ,b) 200 °C , c) 300 °C

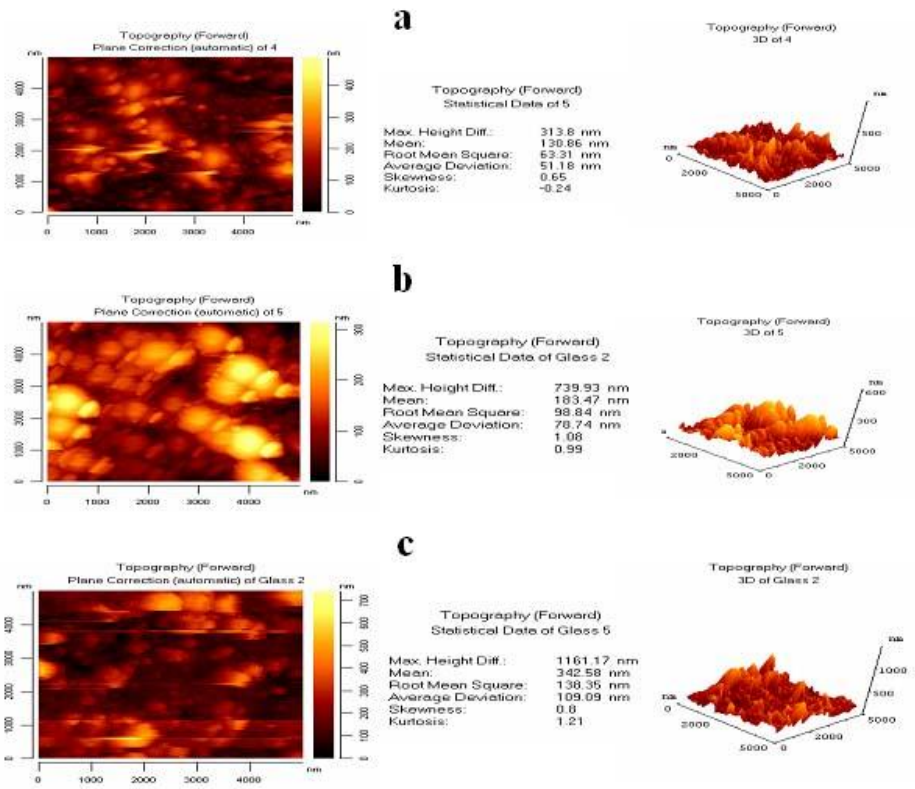


Figure (6) AFM image of CdO film grown at different substrate temperatures on glass a) 100 °C ,b) 200 °C , c) 300 °C

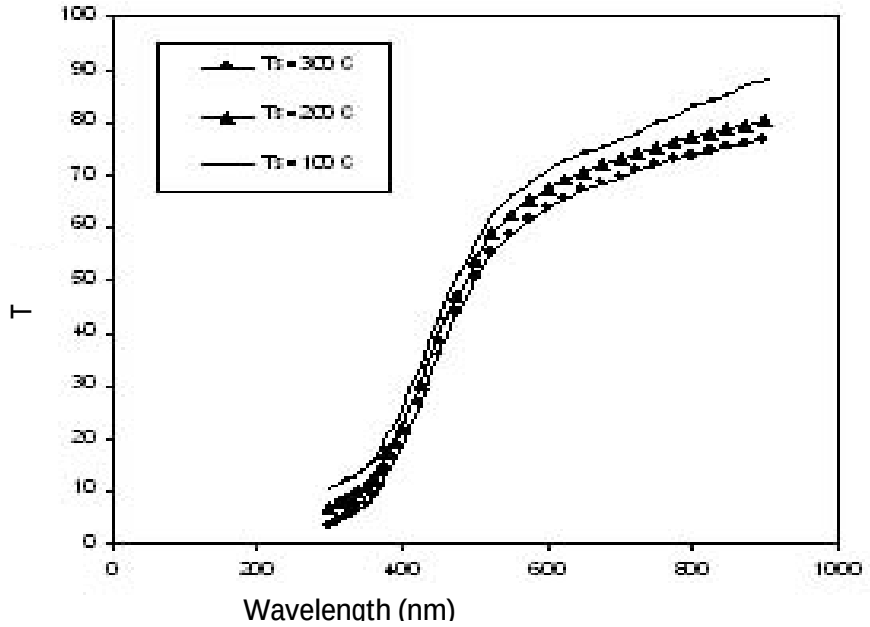


Figure (7) Transmittance spectra of CdO films grown at different substrate temperatures

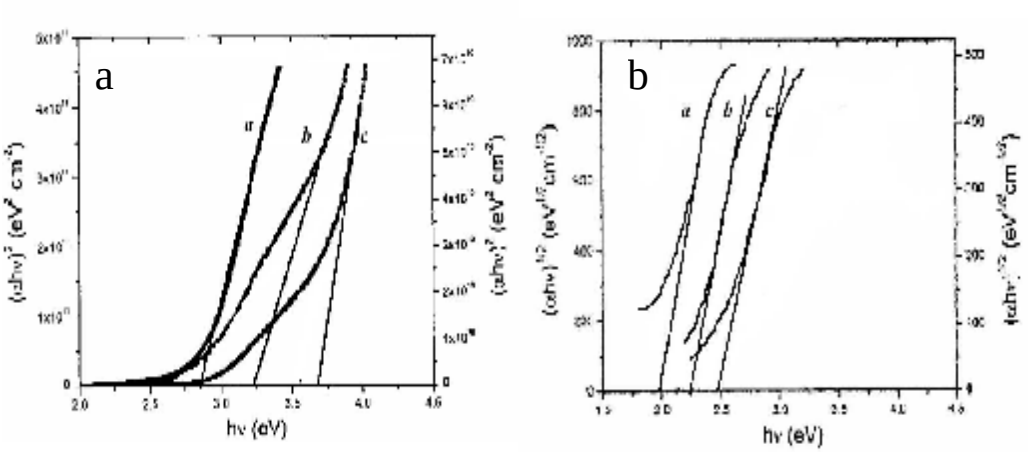


Figure (8) Determination of (a) direct band gap (b) indirect band gap of nanocrystalline CdO thin films for and (c) 300˚C . different substrate temperatures (a) 100˚C, (b) 200˚C,

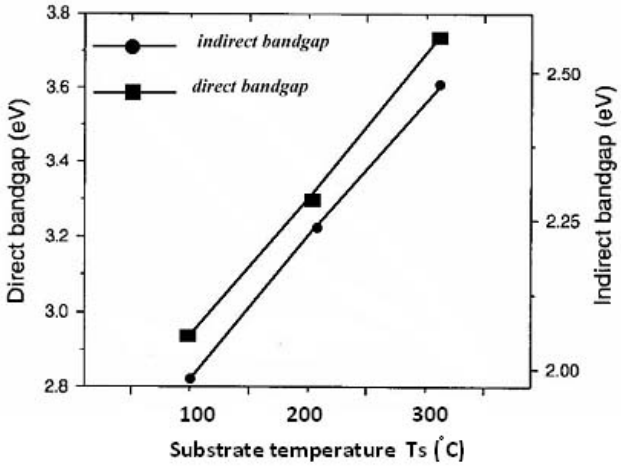


Figure (9) Variation of direct band gap and indirect band gap of nanocrystalline CdO thin film with substrate temperature

Table (1) Comparison of direct bandgap, indirect bandgap ,roughnes,strain and grain size obtained from SEM and grain size obtained from X-ray with different substrate temperature.

Substrate temperature (°C)	*Direct bandgap (eV)*	*Indirect bandgap (eV)*	*Grain size X-ray (nm)*	*Grain size SEM (nm)*	*Roughness (nm)*	*Strain (ε)*
100	*2.81*	*2.00*	*12*	*10*	*63.3*	*0.036*
200	*3.24*	*2.25*	*18*	*17*	*98.8*	*0.032*
300	*3.70*	*2.42*	*47*	*45*	*138.4*	*0.031*