Iraqi Journal of Physics, 2018 *Vol.16, No.38, PP. 112-123*
DOI: 10.20723/ijp.16.38.112-123

Influence of substrates on the properties of cerium -doped CdO nanocrystalline thin films

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Abstract

Transparent thin films of CdO:Ce has been deposited on to glass and silicon substrates by spray pyrolysis technique for various concentrations of cerium (2, 4, and 6 Vol.%). CdO:Ce films were characterized using different techniques such as X-ray diffraction (XRD), atomic force microscopy(AFM) and optical properties. XRD analysis show that CdO films exhibit cubic crystal structure with (11 1) preferred orientation and the intensity of the peak increases with increasing's of Ce contain when deposited films on glass substrate, while for silicon substrate, the intensity of peaks decreases, the results reveal that the grain size of the prepared thin film is approximately (73.75-109.88) nm various with increased of cerium content. With a surface roughness of (0.871–16.2) nm as well as root mean square of (1.06-19.7) nm for glass substrate, while for silicon (84.79-107.48) nm, for a pure CdO and doped with Ce (2, 4, and 6 Vol.%). The 300-nm-thin CdO films showed that the optical energy band gap equal 2.6 eV, and increases with increasing doping until reaches a maximum value of 3.25 eV when doping levels 6 Vol.%.

Key words
CdO thin film, structural, optical properties, XRD.

Article info.
Received: Dec. 2017
Accepted: May. 2018
Published: Sep. 2018

تأثير قواعد الترسيب على خصائص اغشية اوكسيد الكادميوم النانوية CdO الرقيقة المشوبة بالسيريوم Ce

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الخلاصة

تم ترسيب الاغشية الرقيقة الشفافة لـ CdO المشوبة بالسيريوم Ce على قواعد الزجاج والسيليكون بتقنية التحلل الكيميائي الحراري، وبنسب التشويب مختلفة مع السيريوم وكانت (2, 4, and 6 Vol.%). تم التعرف على خصائص الاغشية باستخدام تقنية حيود الأشعة السينية (XRD) ومجهر القوى الذرية (AFM) وكذلك الخصائص البصرية. وبينت فحوصات حيود الاشعة السينية ان اغشية اوكسيد الكادميوم تمتلك تركيب بلوري مكعبي وباتجاه مفضل (111)، وان شدة القمم تزداد مع زيادة تركيز السيريوم عند الترسيب على قواعد الزجاج، اما في حالة الترسيب على قواعد السليكون فان شدة القمم تقل. ومن خلال فحوصات مجهر القوى الذرية في حالة الترسيب على قواعد الزجاج وجد ان الحجم الحبيبي للأغشية المحضرة هي nm (73.75-109.88)، وان الخشونة السطحية هي تقريبا nm (0.871–16.2) وان (RMS) هو nm (1.06-19.7)، اما في حالة الترسيب على قواعد السيليكون تبين ان الحجم الحبيبي هو nm (84.79-107.48) للاغشية النقية والمشوبة. بينت الفحوصات البصرية ان الاغشية ذات سمك (300 nm) وتمتلك فجوة طاقة بصرية (2.6 eV) وان هذه القيمة تزداد مع زيادة نسب التشويب لتصل الى اعظم قيمة لها (3.25 eV) عند نسبة تشويب 6 Vol.%.

Introduction

Transparent Conducting Oxide (TCO) films have been extensively studied because of scientific interest and their potential applications especially in the field of optoelectronic and other solid state devices. CdO is one of the most promising transparent conducting oxides from II to VI group of semiconductors which having high absorption and emission capacity of radiation in the energy gap [1]. This material could be used for different applications such as solar cells [2], temperature controlled in satellites [3], gas sensors [4], photo transistors [5] because of its low electrical resistivity [2], large energy band gap approximately of (2.2 eV) and great luminescence characteristics [5]. Many methods were adopted to grow CdO thin films like vacuum evaporation thermal technique, sol-gel spin coating, spray pyrolysis [6-9]. Between these fabricated methods the spray pyrolysis technique has many privileges such as low cost of the components and raw materials, simplicity and safety [10]. In this technique, characteristics of films relying upon preparation conditions similar to spray rate, nozzle- substrate and the substrate temperature [11]. CdO is one of material considered to be a model n-type semiconductor [12], with cubic structure where each ions collared by six ions of different electric charge [13, 14]. In this work, the variation of the optical, structural properties of CdO thin films obtained by spray pyrolysis method was studied as a function of the Ce doping with various concentrations.

Experimental details

A CdO (pure) and Ce doped thin films at different concentration of Ce (2, 4 and 6 Vol.%), were prepared by chemical spray pyrolysis. The films deposited onto the glass and silicon substrate at deposition temperature of 250± 10 $^{\circ}$C. The substrates were first cleaned with detergent water. The Si wafers were ultrasonically cleaned in distilled water and acetone. Spray solution was prepared by mixing 0.1 M aqueous solutions of CdCl, and $CeCl_4$ at ratio (2, 4 and 6 Vol.%) using a magnetic stirrer . The automated spray solution was then transferred to the hot substrate kept at the normalized deposition temperature of (250 $^{\circ}$C) using filtered air as carrier gas at a flow rate normalized to approximately (2.5) ml/min. To prevent the substrate from excessively cooling, the prepared solution was sprayed on the substrate for 10 s with 15 s intervals. The films had a uniform thickness of range (300) nm. The structural properties were determined by X-ray diffraction (XRD; Shimadzu) with CuKα radiation (λ= 0.15406 nm). Film morphology was analyzed by atomic force microscope (AFM) type- (CSPM).The optical absorption and transmission spectra were obtained using a UV-VIS spectrophotometer 6800 JENWAY, Germany) within the wavelength range of (200-1100) nm.

Result and discussion

Structural Properties

The XRD patterns of CdO thin films grown from different concentration (2, 4 and 6 Vol.%) of Ce ranging deposited on glass and silicon substrate are show in Figs.1 and 2. These patterns show sharp and narrow diffraction peaks suggesting the films display good crystallinity. The X-ray diffraction profiles reveal that the films are polycrystalline in nature with cubic structure. All the films have preferential orientation along the (111) plane irrespective of different substrate. Our previous work on CdO thin films prepared by the spray pyrolysis technique showed a similar structure with a preferential orientation along the (111) plane [6]. The intensity of the peaks (111), (200), (220) and (311) at angle (2Θ) at angle 33.11°, 38.33°, 55.38°, 65.83° deposited on glass substrate but decreases with silicon substrate. The other prominent peaks in the XRD pattern corresponds to the planes (200), (220), (311) and (222) according to the JCPDS card No. 75-0594 by Beevi et al. [15]. The preferential orientations of the films were evaluated by calculating the preferential orientation factor (hkl) from the X-ray data by a method reported earlier [14]. The variation in preferential orientation factor (h k l) for the (1 1 1) and (2 0 0) planes as a function of different substrate is shown in Fig.1. a and b Where the intensity of the XRD is higher in the case of glass. The results revealed that different substrate influences the structural properties of the CdO films. The mean crystallite size calculated using Scherrer formula for glass and silicon substrate of CdO is found decreasing with increase in doping concentration to be 67-29 nm for glass, while in the case of Silcon it is increase with a greater concentration of the doped 24-58 nm respectively is used to calculate the crystallite size (D) of the as deposited samples [16]:

$$D = \left(\frac{K\lambda}{w \cos\theta} \right) \tag{1}$$

where D is the crystallite size, *K* is a constant equal 0.94, λ is the wavelength and *w* is the full width at half maximum (FWHM) of diffraction peak measured in radians and θ is the Bragg angle.

Morphological properties

Atomic force microscopy (AFM) is a non-invasive and convenient technique to study the morphological characteristics and surface roughness of semiconductor thin films and to observe microstructure of thin films. It is well known that AFM is one of the most effective ways for the surface analysis due to its high resolution and powerful analysis software [17] Fig.3 and 4, show two-dimensional (2D) and three- dimensional AFM scans of the crystallized CdO and CdO:Ce thin films grown by spray pyrolysis on glass and silicon substrate respectively, AFM analysis for pure CdO film showed good uniformity revealing and uniform growth of the films, the figures show the a surface become smooth when doping at rare earth compared to the CdO film. The small spherical grains agglomerates are uniformly distributed of shape and size along the film surface, It can be seen that the film is crack-free and quite smooth with a decrease on the surface roughness [18]. Fig. 3 shows smoothening surface for films deposited on glass substrate may be due to order of surface atoms to attain lower energy state. This films have a high grain density distribution with tightly packed grains, and it is exhibits a lower surface roughness with uniform oriented. This may be correspond to the columnar structure which is associated with the (111) CdO textured growth [18]. Furthermore, the grain size, Root mean square and roughness of the samples decreases with increase in doping concentration are shown in Figs. 5-10 and Tables1 and 2, respectively.

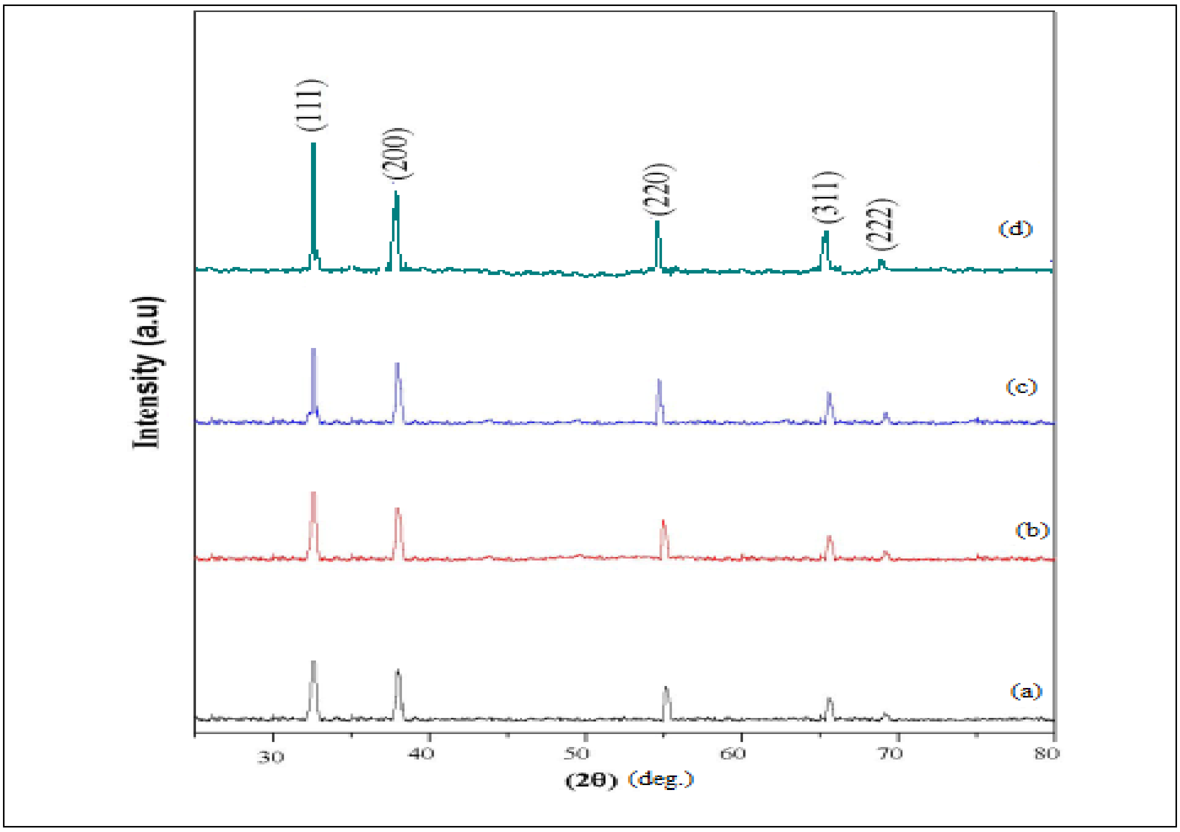

Fig. 1: XRD pattern of a) pure CdO films b) 2%Ce, c) 4%:Ce, and d) 6% Ce deposited on glass substrate.

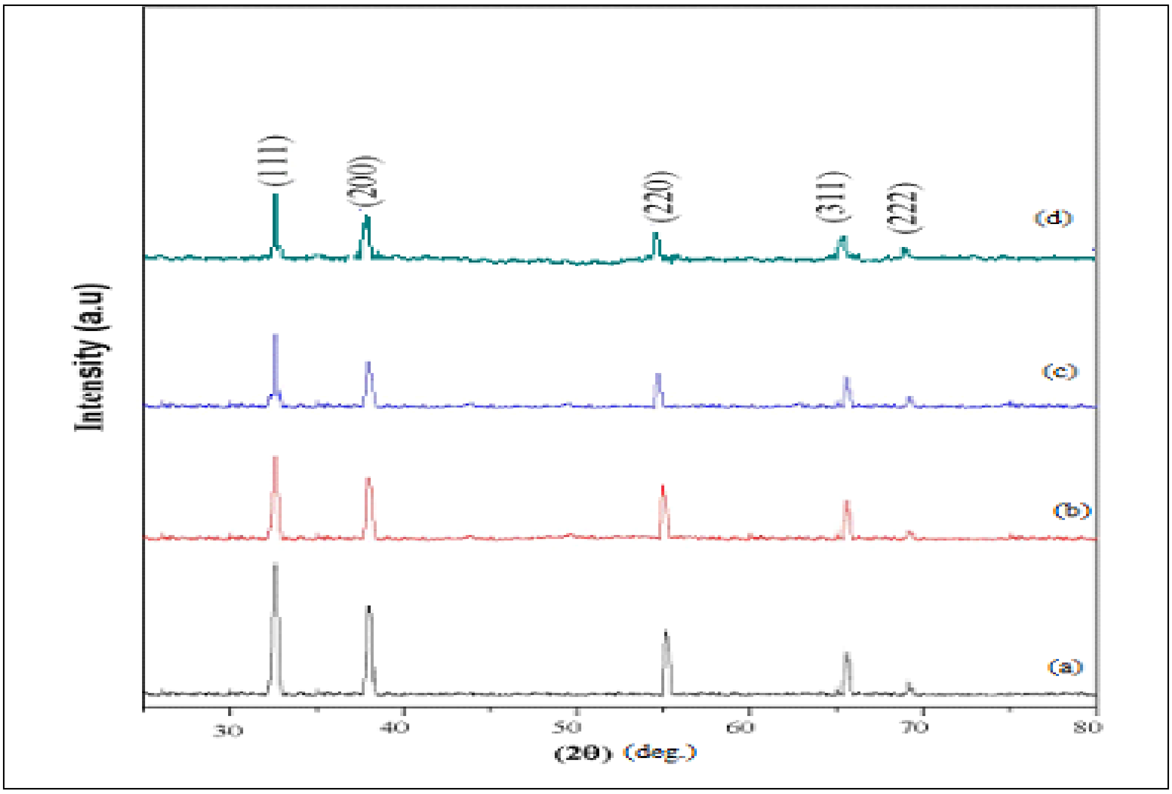

Fig. 2: XRD pattern of a) pure CdO films b) 2% Ce, c) 4%:Ce, and d) 6% Ce deposited on silicon substrate.

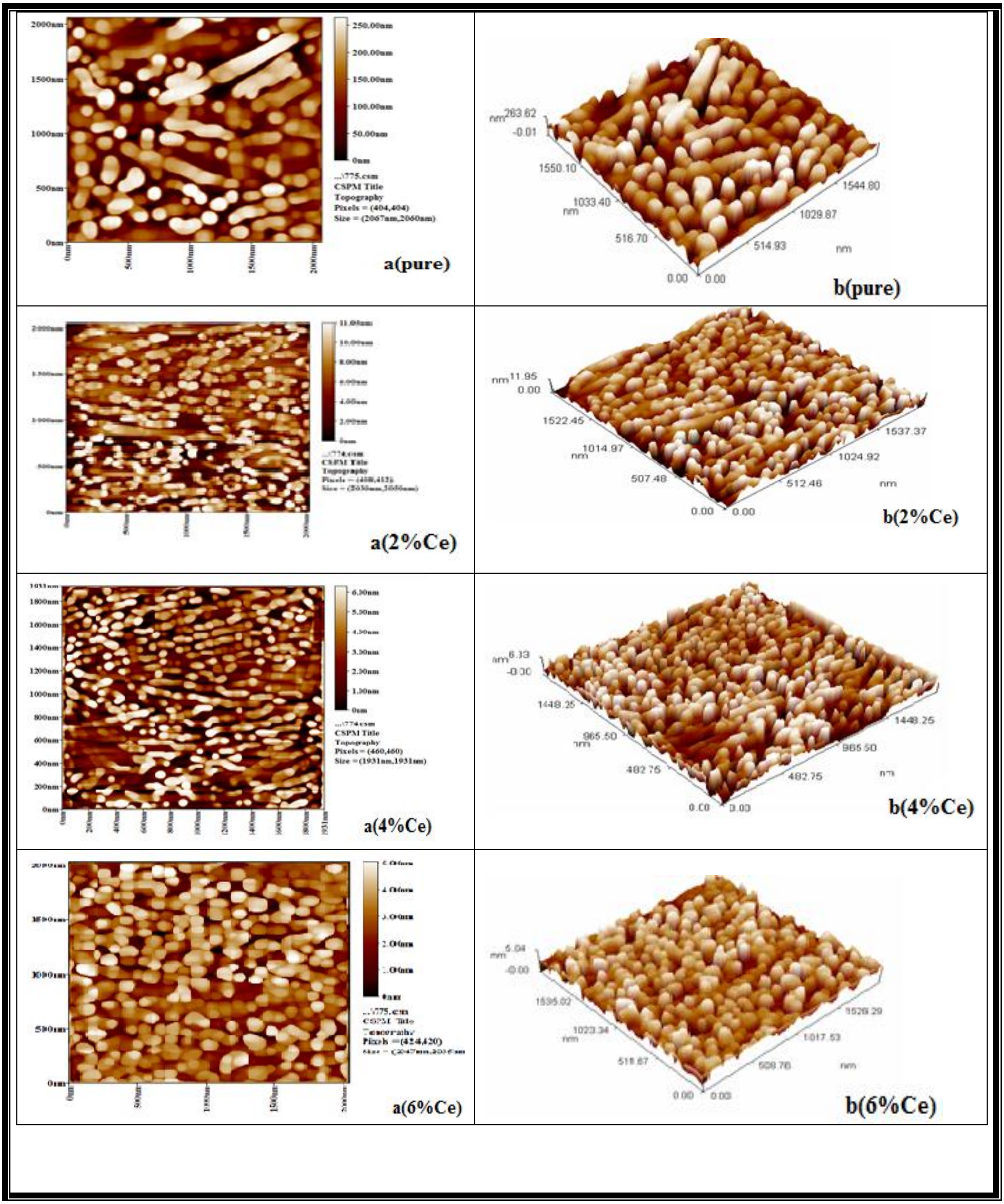

Fig. 3: AFM images (a) 2-D and (b) 3-D of prepared CdO films for on glass substrates at different concentration of Ce.

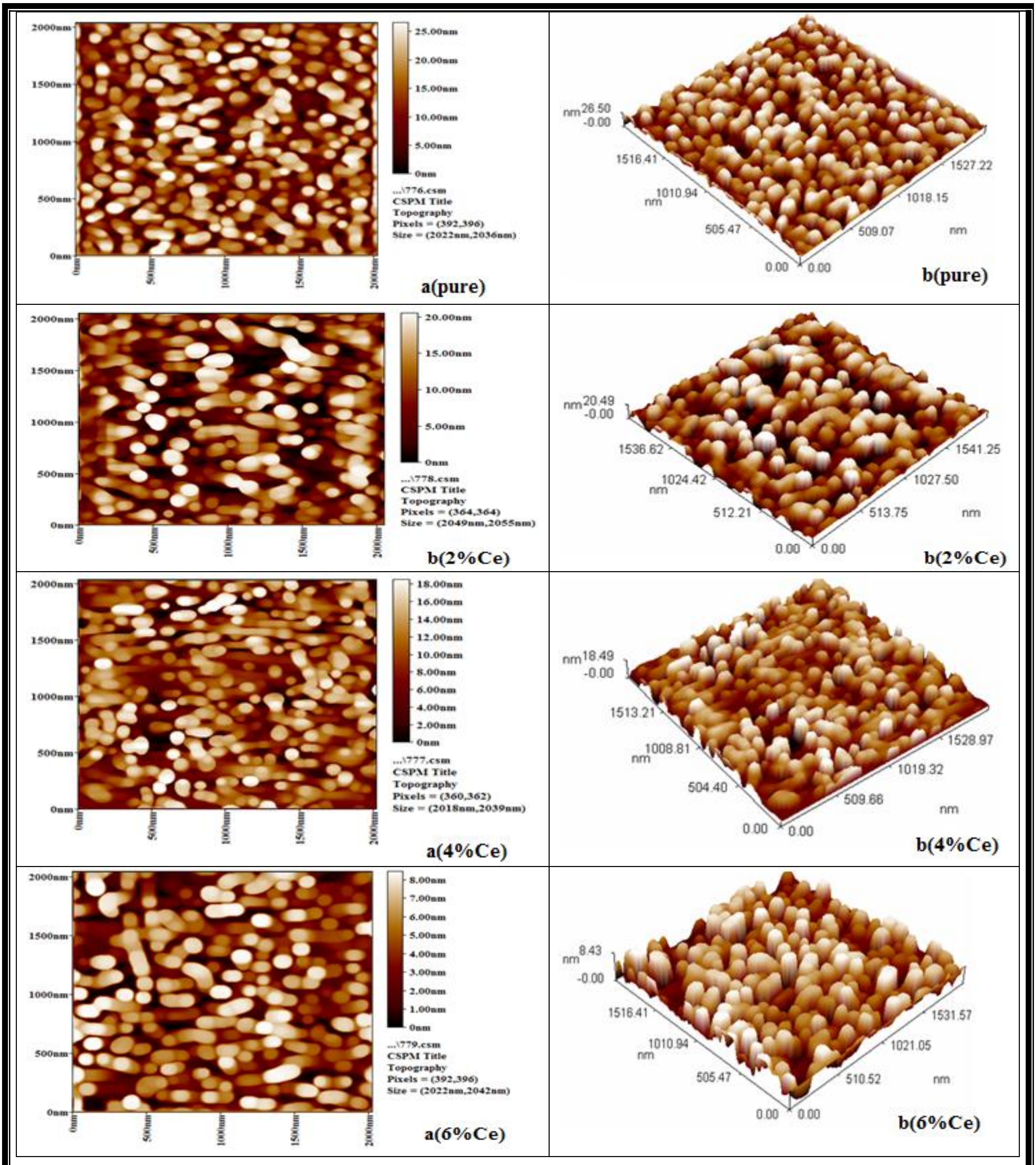

Fig. 4: AFM images (a) 2-D and (b) 3-D of prepared CdO films for on silicon substrates at different concentration of Ce.

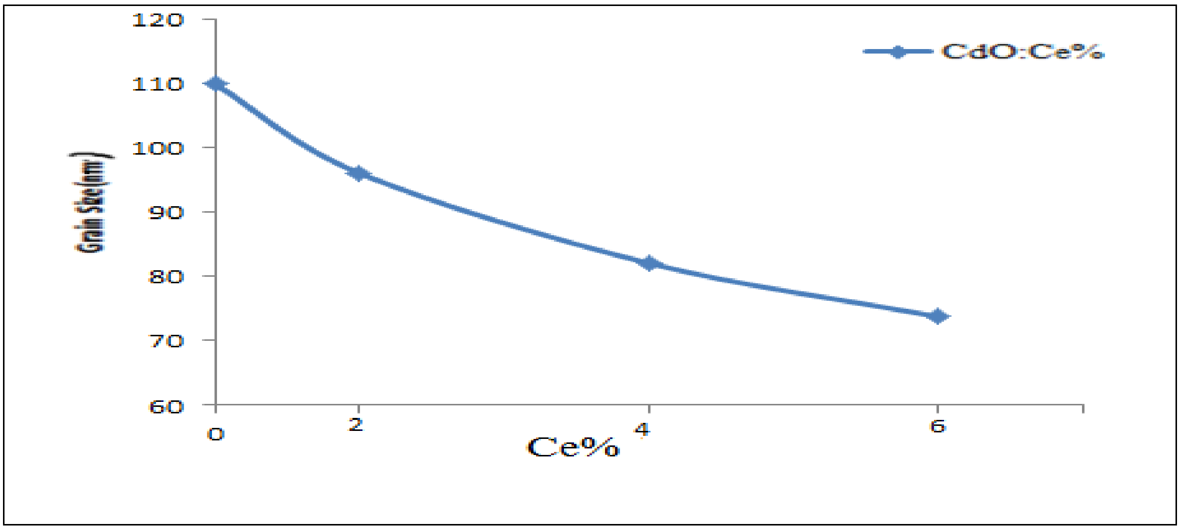

Fig. 5: Variation in grain size with Ce concentration for CdO prepared glass substrates.

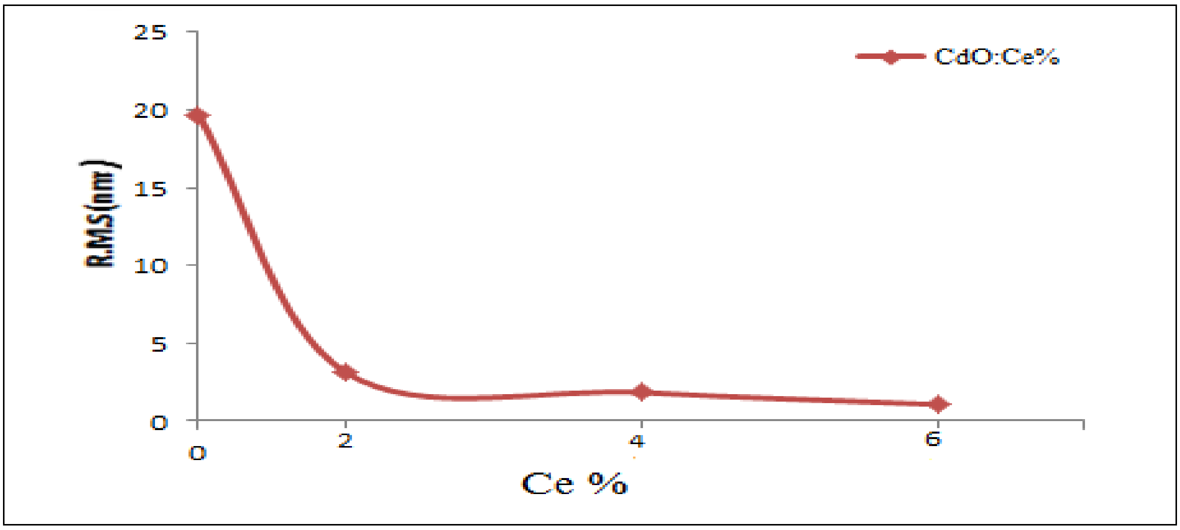

Fig. 6: Variation of Root mean square with Ce concentration for CdO prepared glass substrates.

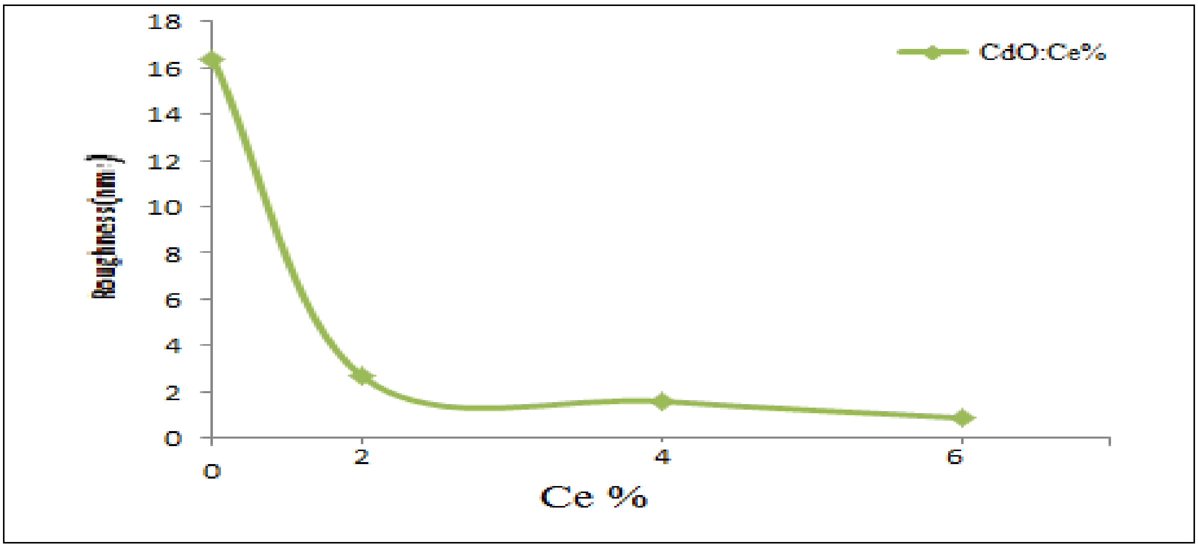

Fig. 7: Variation of roughness with Ce concentration for CdO prepared glass substrates.

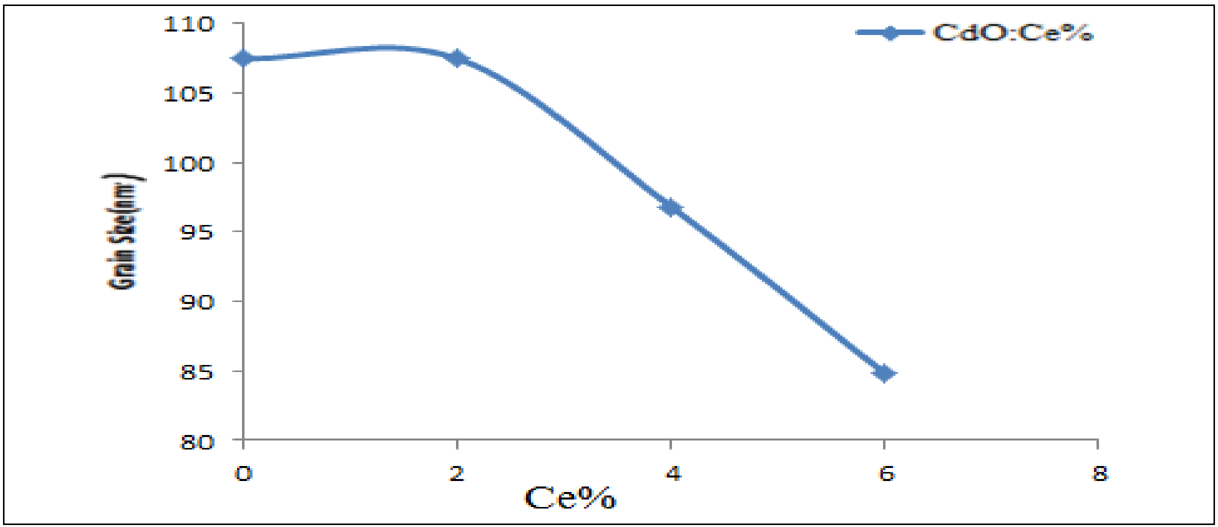

Fig. 8: Variation of grain size with Ce concentration for CdO prepared silicon substrates.

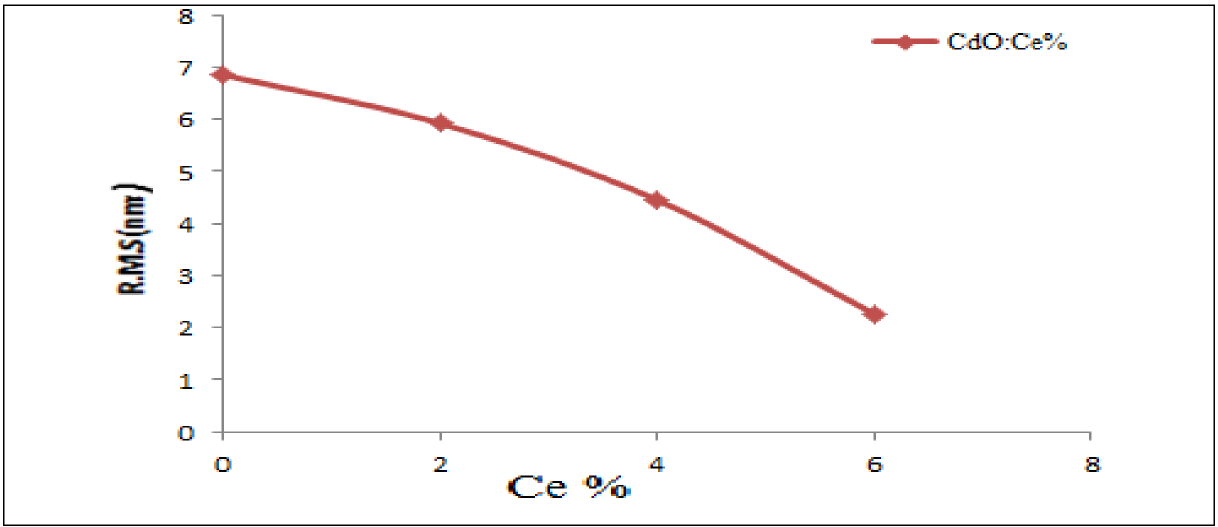

Fig. 9: Variation of Root mean square with Ce concentration for CdO prepared silicon substrates.

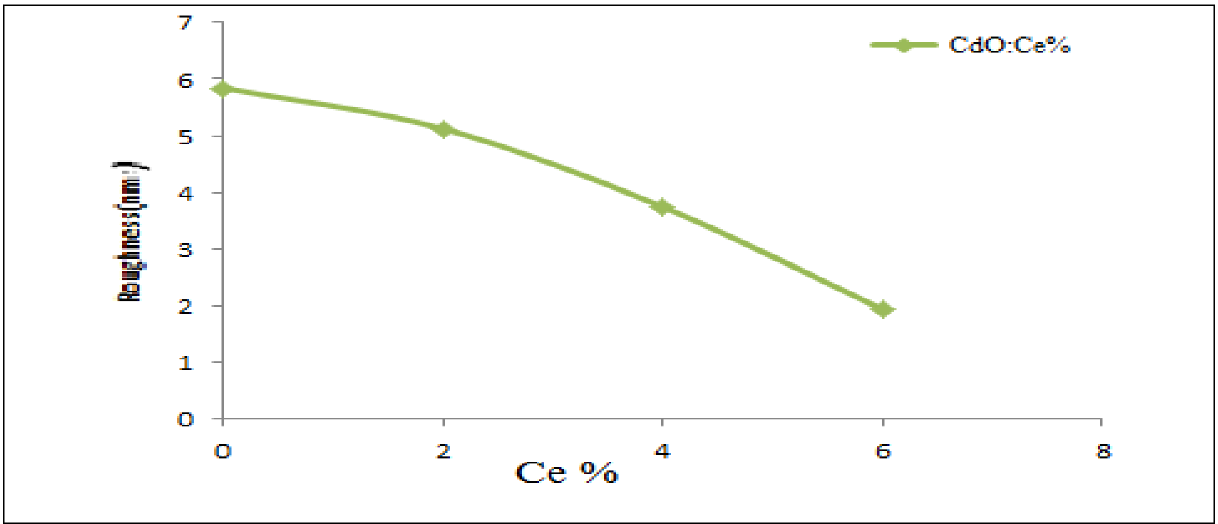

Fig. 10: Variation of roughness with Ce concentration for CdO prepared silicon substrates.

Table 1: The average grain sizes and roughness average for CdO prepared on glass substrates.

Doping ratio	Average Grain sizes from AFM (nm)	Root mean square (nm)	Roughness Average (nm)
(Pure)	109.88	18.7	16.2
2 vol.%	96.00	3.11	2.65
4 vol.%	82.03	1.83	1.58
6 vol.%	73.75	1.06	0.871

Table 2: The average grain sizes and roughness average for CdO prepared on silicon substrates.

Doping ratio	Average Grain sizes from AFM (nm)	Root mean square (nm)	Roughness Average (nm)
(Pure)	107.48	6.85	5.84
2 vol.%	107.48	5.92	5.12
4 vol.%	96.80	4.45	3.74
6 vol.%	84.79	2.26	1.93

Optical properties

The transmittance spectrum (T) of CdO and CdO:Ce thin films at different concentration of Ce (2, 4, 6) Vol% is shown in Fig.11. It is clear from this figure that the transmittance increases with increasing of Ce concentration [19]. The absorption coefficient (α) of CdO and CdO:Ce thin films, was determined by using Eq.(2) [20].

$$\alpha = 2.303\frac{A_o}{t} \tag{2}$$

where A_o is the absorption, t is thickens. The variation of the absorption coefficient of CdO and CdO:Ce thin films with the wavelength at different concentration of Ce (2, 4 and 6) Vol % is shown in Fig. 12. It can be noticed that the value of the absorption coefficient of CdO thin films is of the order of (10^4) cm^{-1} which supports the direct band gap nature of the semiconductor [20]. It is also clear that the absorption coefficient of CdO and CdO:Ce thin films decreases with the increasing Ce concentration. This is attributed to the decrease in the absorbance of the films with the increase in Ce concentration causing an decrement in their absorption coefficient where the relation between the absorbance and absorption coefficient is proportional at constant thickness according to Eq.(2).

The optical energy gap values (E_g) for CdO:Ce thin films prepared by chemical spray pyrolysis method have been determined from the region of the high absorption at the fundamental absorption edge of these films by using Tauc equation [21].

$$(\alpha h\nu) = A^*(h\upsilon - Eg)^r \tag{3}$$

where, r is the transition types, hυ: is the incident photon energy in eV, A^*: is a constant depends on the nature of the material.

This equation is used to find the type of the optical transition by plotting the relations $(\alpha h\upsilon)^2$, $(\alpha h\upsilon)^{1/2}$, $(\alpha h\upsilon)^{2/3}$ and $(\alpha h\upsilon)^{1/3}$ versus photon energy (hυ) and select the optimum linear part[19]. The first relationship was found to lead to a written adoption, which describes the permitted direct transition, then E_g was determined by the extrapolation of the portion at (α=0) as shown in Fig. 13. It is clear that the optical energy gap for CdO and CdO:Ce thin films increases as the Ce concentration in the films increased [22]. The optical energy gap values for CdO and CdO:Ce thin films were (2.55, 2.75, 2.95 and 3.25) eV for Ce concentration (0, 2, 4 and 6) Vol% respectively for Table 3. The increase in the energy gap values may be caused by the decrease in crystal size as shown in the tests of the X-ray data.

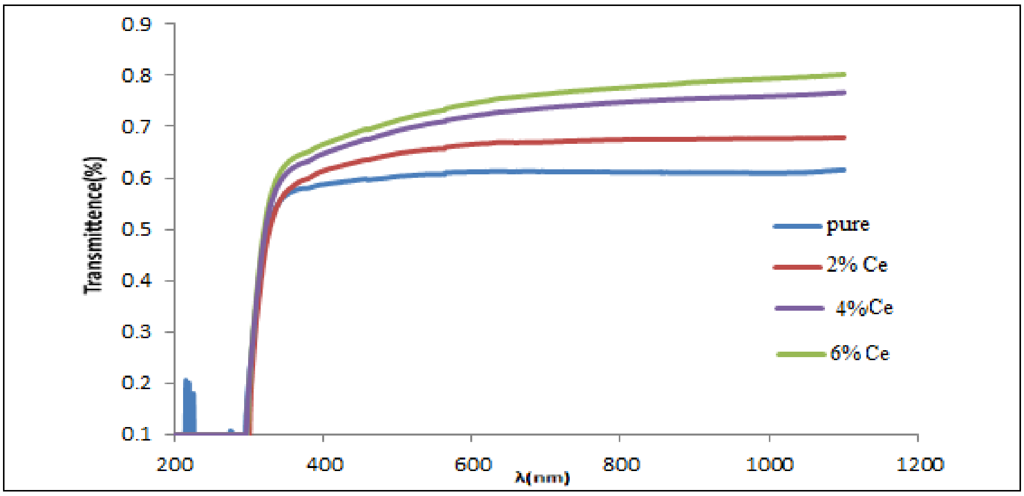

Fig. 11: Transmittance spectra of CdO thin films at different concentration of Ce.

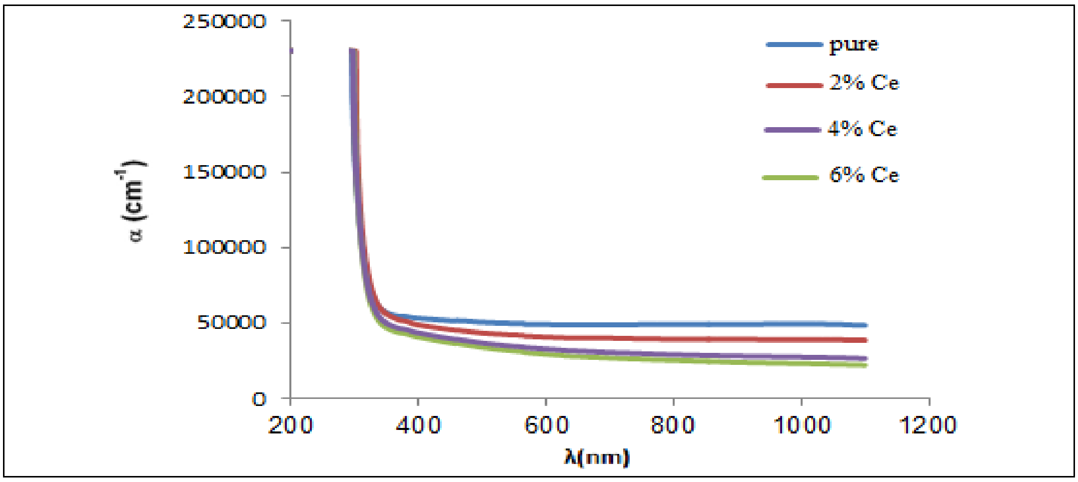

Fig. 12: Variation of absorption coefficient as a function of wavelength for CdO films at different concentration of Ce.

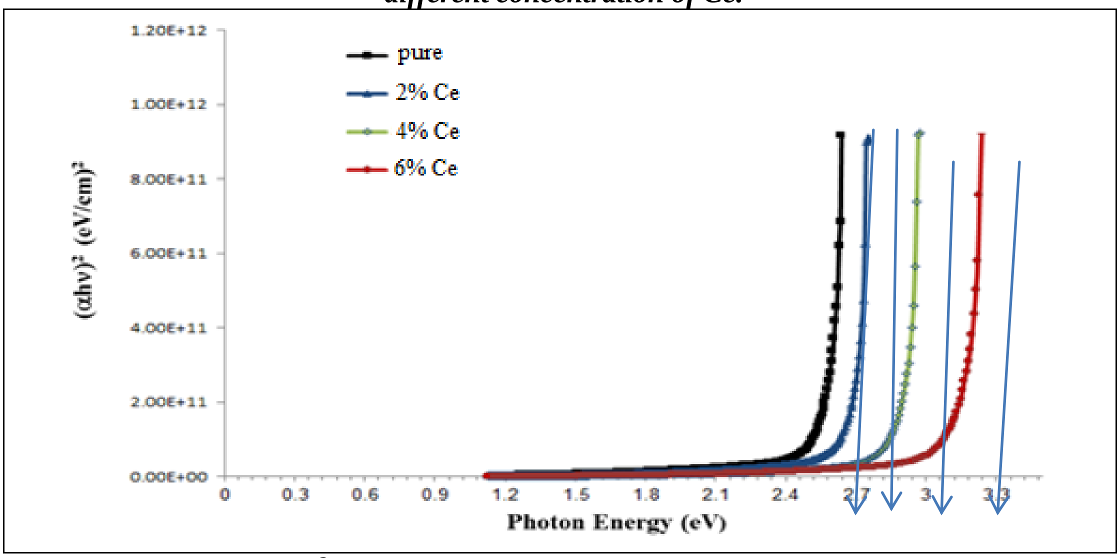

Fig. 13: Plot of $(\alpha h\nu)^2$ versus $h\nu$ for CdO thin film at different concentration of Ce.

Table 3: The optical energy gap average for CdO prepared.

Doping ratio	Energy gap (E_g) eV
(Pure)	2.55
2 vol.%	2.75
4 vol.%	2.95
6 vol.%	3.25

Conclusions

Highly transparent and conductive CdO films were deposited on glass substrates by using spray pyrolysis. Transparent and conducting CdO films prepared at a substrate temperature of 450 °C were identified as CdO with a preferred (111) orientation. The structural, optical properties of these films were investigated as a function of the Cerium doping concentration. The X-ray diffraction shows the polycrystalline nature of as deposited films and exhibit cubic crystal structure and the intensity of the peak increases with increasing Ce-doping concentration for glass substrate, while for silicon the intensity of peaks decrease. The AFM images show homogenous grain and smoothing films. The transmittance value increases with increasing Ce-doping concentration. The band gap energy value increases with increasing Ce-doping concentration.

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