Structural and optical properties of CdO and $CdO_{0.99}Cu_{0.01}$ thin films prepared by pulsed laser deposition technique

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Abstract

Structural and optical properties of CdO and $CdO_{0.99}Cu_{0.01}$ thin films were prepared in this work. Cadmium Oxide (CdO) and $CdO_{0.99}Cu_{0.01}$semiconducting films are deposited on glass substrates by using pulsed laser deposition method (PLD) using SHG with Q-switched Nd:YAG pulsed laser operation at 1064nm in $6x10^{-2}$ mbar vacuum condition and frequency 6 Hz. CdO and $CdO_{0.99}Cu_{0.01}$ thin films annealed at 550 Č for 12 min. The crystalline structure was studied by X-ray diffraction (XRD) method and atomic force microscope (AFM). It shows that the films are polycrystalline. Optical properties of thin films were analyzed. The direct band gap energy of CdO and $CdO_{0.99}Cu_{0.01}$ thin films were determined from $(\alpha h\upsilon)^{1/2}$ vs. photon energy curve and found to be 2.3 eV for CdO thin film, comparing with that the $CdO_{0.99}Cu_{0.01}$film which found to be 2.2eV. The electrical measurements shows that the conductivity and mobility of the charge carriers increase when Cu doped CdO.

Key words

PLD, Cadmium Oxide, optical properties.

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الخصائص التركيبية والبصرية لأغشيه CdO و $CdO_{0.99}Cu_{0.01}$ و المحضرة بتقنية ترسيب الليزر النبضي

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الخلاصة

في هذا البحث تمت دراسة الخصائص التركيبية و البصرية للأغشية الرقيقة CdO و $CdO_{0.99}Cu_{0.01}$. حيث تم ترسيب أغشية أُكسيد الكادميوم (CdO) و $CdO_{0.99}Cu_{0.01}$ على ركائز من الزجاج بواسطة تقنية ترسيب الليزر النابضي (PLD) باستخدام SHG مع Q-switched ليزر نبضي 1064 nm في $6x10^{-2}$ mbar حالة الفراغ وبتردد 6 هيرتز. وتم تلدين الاغشية المحضرة CdO و $CdO_{0.99}Cu_{0.01}$عند درجة حرارة 550 درجة مئوية و لمدة 12 دقيقة. تمت دراسة البنية البلورية لحيود الأشعة السينية (XRD) و مجهر القوة الذرية (AFM) مما دل على ان نمو الاغشية المحضره بشكل متعدد التبلور. كما تم تحليل الخصائص البصرية للأغشية الرقيقة وتحديد فجوة الطاقة المباشرة للاغشية Cdo و $CdO_{0.99}Cu_{0.01}$ من رسم العلاقه بين $(\alpha h\upsilon)^{1/2}$ مقابل منحنى طاقة الفوتون و وجدت ان فجوة الطاقة مساوية الى2.3 eV لأغشية CdO، مقارنة مع لأغشية $CdO_{0.99}Cu_{0.01}$ والتي وجدت انها مساويه الى 2.2eV. كما بينت القياسات الكهربائية ان التوصيلية وتحركية نواقل الشحنه تزداد في حالة تشويب اوكسيد الكادميوم CdO بمادة النحاس مادة النحاس Cu.

Introduction

Cadmium (Cd) is a soft, ductile, silver-white metal that belongs together with zinc and mercury to group IIb in the Periodic Table. It has relatively low melting (320.9 °C) and boiling (765 °C) points and a relatively high vapour pressure. In the air cadmium is rapidly oxidized into cadmium oxide, cadmium oxide is used in batteries, electroplating baths, pigments, plastics, synthetic products[1].

Cadmium Oxide (CdO) attracts a great attention due to its electrical and optical properties. CdO is an n-type semiconductor with direct band gap at approximately 2.3eV. The wide band gap properties of semiconductors, like CdO, are of interest particularly for optoelectronic applications in transparent conducting oxides (TCO), solar cells, smart windows, optical communications, flat panel displays, photo-transistors, as well as other types of applications like IR heat mirror, gas sensors, low-emissive windows, thin film resistors, etc. [2-5].

There are several methods developed for the synthesis of CdO films such as spraypyrolysis [6,7], sputtering, chemical bath deposition(CBD), pulsed laser deposition, MOCVD, sol-gel spin coating method and thermal evaporation technique [8].

Pulsed laser deposition has become a widely used deposition technique for thin film growth. PLD presents several advantages with respect to other deposition techniques. In fact, due to the high energetic content of the ejected species, it allows low temperature deposition process. Moreover, its ability to congruently transfer the stoichiometry from the target to the films, allows the growth of complex materials. The technique is based on the vaporization process induced by focusing a high energy pulsed laser on the surface of the material. When the energy laser density is higher than a threshold value, which depends both on the material and the laser wavelength, a stream of atoms, mecules, and clusters is ejected from the target surface. Such a stream, known as a plume and being also composed of excited neutral and ionized species, emits radiation [9].

In this work pure CdO and Cu doped CdO films were deposited on glass and Silicon substrates by pulse laser deposition. The electrical, structure and optical properties were studied.

Experimental procedure

(0.01 wt %) Cu-doped CdO target for PLD was prepared by solid-state reaction method. The pulsed laser deposition experiment was carried out inside a locally designed vacuum chamber at pressure (10^{-5} mbar) and ablated by a second harmonic generation (SHG) with Q-switched Nd:YAG pulsed laser operated at 1064nm. Pulse width 10nsec repetition frequency 6Hz and operated at 700mJ energy to generate plasma plume. Prior to deposition, glass substrates were cleaned in deionized water, and finally dried. In order to get a uniform film thickness, substrates were keptrotating during the deposition. The films were deposited on glass substrates with rate of deposition equal 0.5 nm/sec. All samples were annealed at 550 $\mathring{C}$ to enhancement the structure of the samples. The thickness of the prepared film was measured by laser interferometer technique. The thickness of the film determined by this procedure is about 500nm. The structure of the film was obtained using X-ray diffraction (XRD) method (Shimadzo 6-2006, with Cu-Kα radiation having wavelength λ= 1.5406 A^{O}). Microstructure surface topography was examined using (AFM).Optical transmittance was recorded with a double beam Shimadzu UV-Visible spectrophotometer in the wavelength range 200-800 nm. The Hall measurement was determined by using HMS3000 Hall measurement setting.

Results and discussion

The XRD spectrum of CdO and $CdO_{0.99}Cu_{0.01}$films grown on the glass substrates are shown in Fig. 1. Three strong diffraction peaks are observed for planes (111), (200) and (220). The presence of different peaks in the figure shows that the films are polycrystalline in nature with preferential orientation along the (111) crystal plane. The results shown that the planes are enhanced in the $CdO_{0.99}Cu_{0.01}$ films. The comparison of observed 2θ, d, I/I_o and (hkl) values for CdO and $CdO_{0.99}Cu_{0.01}$ thin films are shown in Table 1.

There are no additional peaks without Cu upon doping indicates the solubility of the dopant in the crystal structure. This result is comparable with results obtained by [7, 10 and 11].

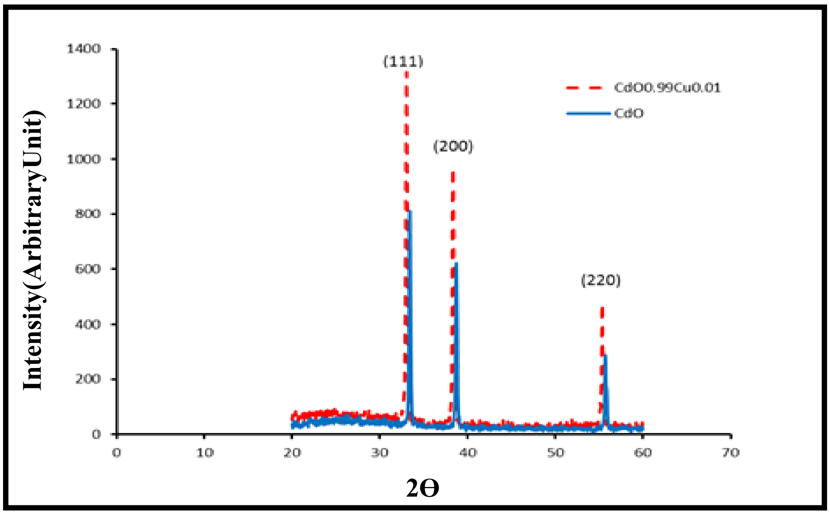

Fig.1: X-ray diffraction pattern of CdO and$CdO_{0.99}Cu_{0.01}$ thin films.

Table 1: Comparison of 2θ, d, I/I_o and (hkl) values of CdO and $CdO_{0.99}Cu_{0.01}$ thin films.

Peak no.	2θ		d spacing (10^{-10}m)		I/I_o		hkl
	CdO	$dO_{0.99}Cu_{0.01}$	CdO	$dO_{0.99}Cu_{0.01}$	CdO	$CdO_{0.99}Cu_{0.01}$	
1	33.4552	33.o755	2.6763	2.70616	100	100	111
2	38.7497	38.3700	2.3219	2.34405	81	80	200
3	55.7293	55.3771	1.64811	1.65775	41	40	220

AFM images (2D and 3D) were prepared of the CdO and $CdO_{0.99}Cu_{0.01}$thin films on glass substrates as shown in Fig.2a and b. Fig.2a shows that Roughness average is about 4.31 nm and the Root Mean Square about 5.4nm while Fig.2b shows that Roughness average is about 2.61nm and root mean square about 3.15nm. The grain analysis report which estimated for CdO and $CdO_{0.99}Cu_{0.01}$ thin films and the average diameter of the particles about 98.65nm and 87.37nm are illustrated in Fig.3a and b; respectively.

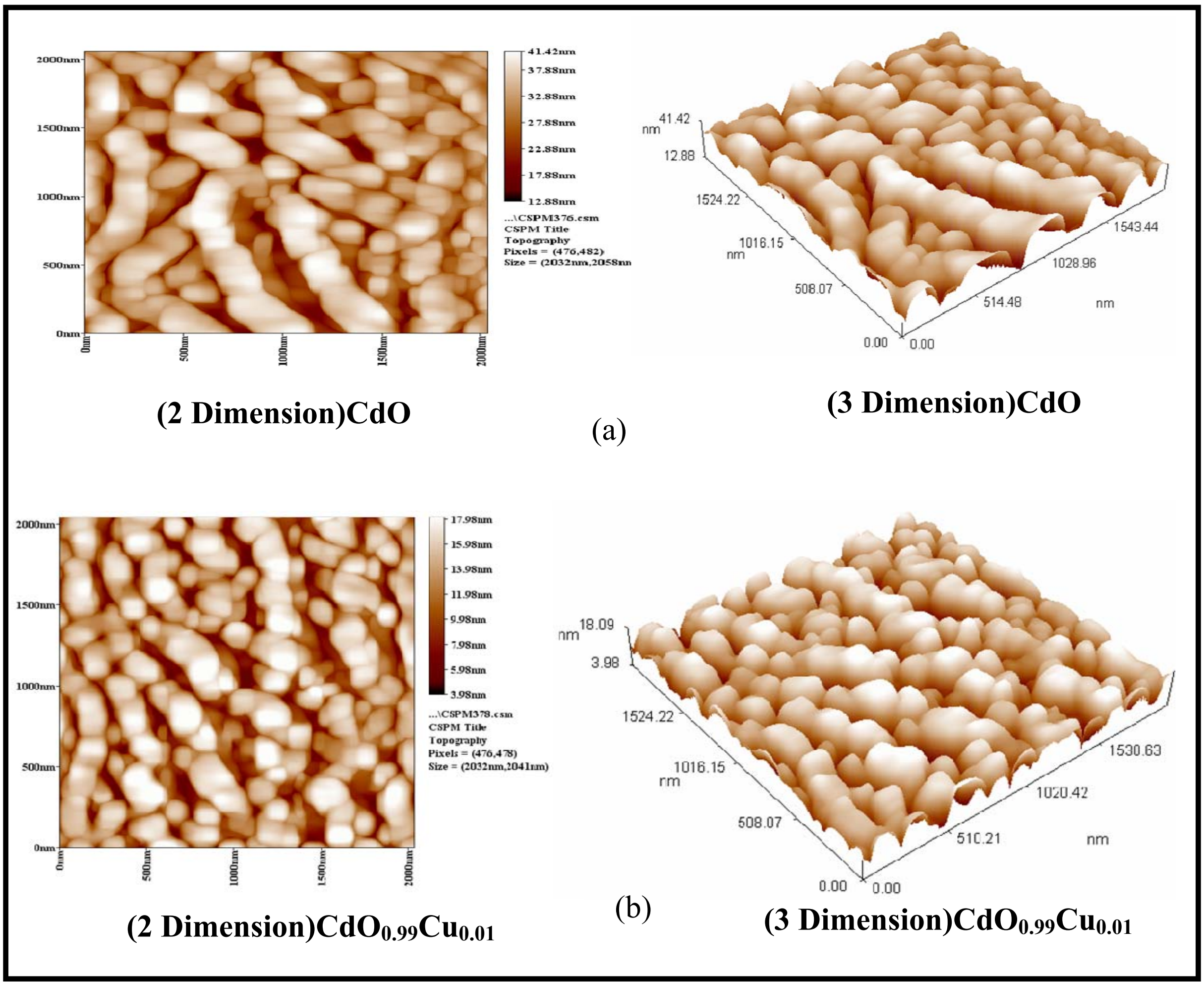

Fig.2a, b: AFM images (2D and 3D) of CdO and $CdO_{0.99}Cu_{0.01}$thin films.

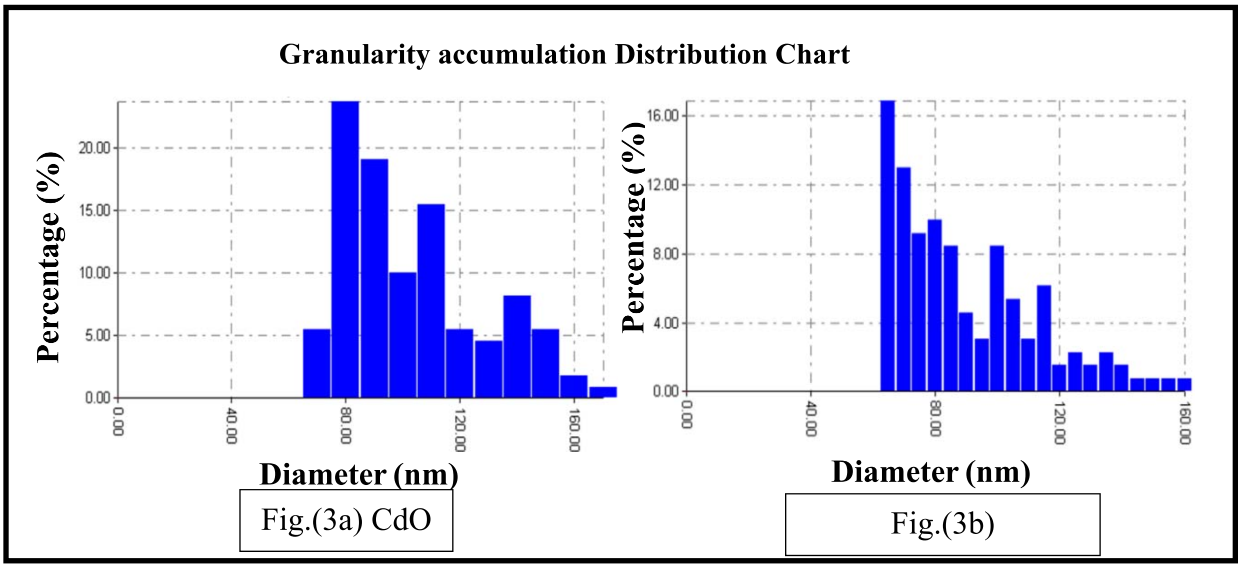

Fig.3a, b: AFM grain analysis report for the CdO and $CdO_{0.99}Cu_{0.01}$ thin films of 500 nm thickness.

The absorption spectrum of CdO and $CdO_{0.99}Cu_{0.01}$thin films with thickness 500nm is shown in Fig.4. The figure shows high absorption coefficient in the UV region, whereas it is transparent in the visible region for CdO film, and it is increasing and shifted toward the visible region for $CdO_{0.99}Cu_{0.01}$ film.

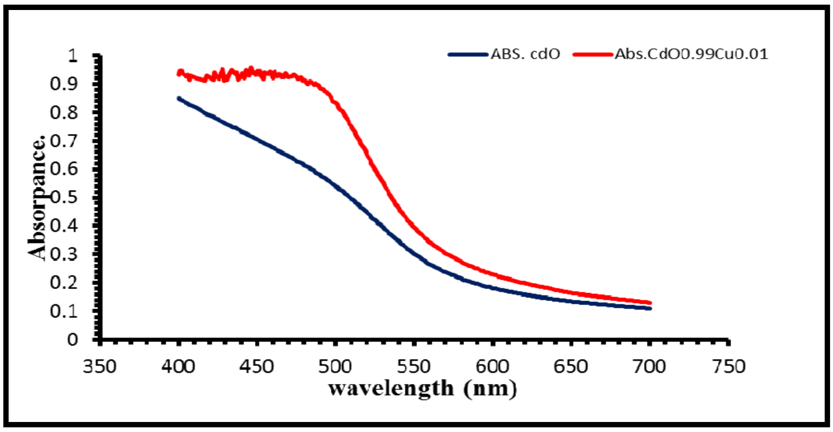

Fig.4: Absorpance spectrum of CdO and $CdO_{0.99}Cu_{0.01}$ thin films.

Fig.5 estimated the optical transmittance spectra with wavelength from (400-750nm) of the CdO and $CdO_{0.99}Cu_{0.01}$ thin films. It is observed from this figure that the films show high transmission in the visible region and low transmission in the UV region. The optical transmittance increases for $CdO_{0.99}Cu_{0.01}$ film.

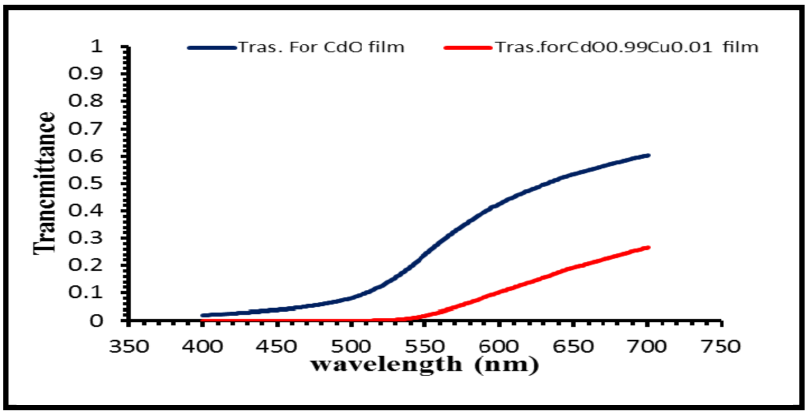

Fig. 5:Transmittance spectrum of CdO and $CdO_{0.99}Cu_{0.01}$ thin films.

The reflectance (R) has been found by using the relationship:

$$R+T+A=1 \qquad (1)$$

where (A) is the absorption and (T) is the transmission. Fig.6 shows the reflectance spectra for the CdO and $CdO_{0.99}Cu_{0.01}$ thin films as a function of wavelength. It is clear from this figure that the reflectance of the films increased with the increasing of the wavelength for $CdO_{0.99}Cu_{0.01}$ thin film, while decreased for CdO thin film at wavelength in the range 590-750 nm.

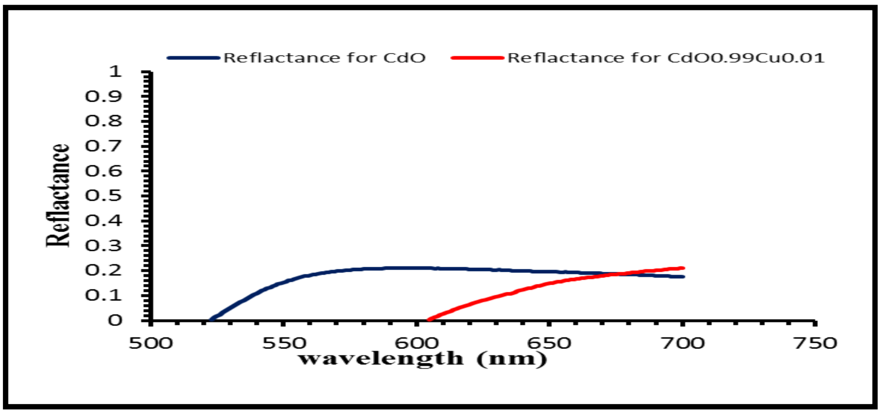

Fig.6: Reflectance of CdO and $CdO_{0.99}Cu_{0.01}$ thin films.

Assuming direct transition, the dependence of $(\alpha h\upsilon)^2$ on the photon energy ($h\upsilon$) is plotted following Tauce relation[11,12] and the graph is illustrated in Fig.7. The extrapolation of the linear part of the above plot to $(\alpha h\upsilon)^2=0$ gives the energy gap values of the CdO and $CdO_{0.99}Cu_{0.01}$films, which were found to be about 2.3eV and 2.2eV respectively. It can be noticed from this figure that the value of energy gap is decreasing for $CdO_{0.99}Cu_{0.01}$film. These values are in a good agreement with the values presented by other workers[13].

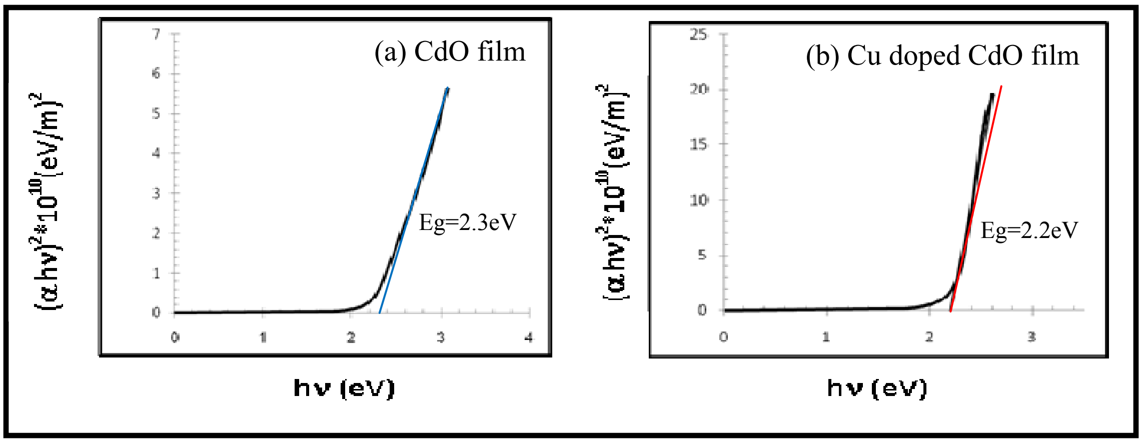

Fig. 7: The $(\alpha h\upsilon)^{\wedge 2}$ as a function of Photon energy ($h\upsilon$) of (a)CdO and (b) $CdO_{0.99}Cu_{0.01}$ thin films.

The refractive index (n) is an important parameter for optical materials and applications. Thus, it is important to determine optical constants of the films. The refractive index of the films was determined from the following relation[14]:

$$n = \left(\frac{1+R}{1-R}\right) + \sqrt{\frac{4R}{(1-R)^2} - k^2} \qquad (2)$$

where k is the extinction coefficient ($k=\alpha\lambda/4\pi$). Fig. 8 shows the variation of the refractive index as a function of the wavelength for both CdO and $CdO_{0.99}Cu_{0.01}$thin films, which indicate that the refractive index increases with increasing of wavelength for $CdO_{0.99}Cu_{0.01}$ thin film, because the refractive index is a function of wavelength, while decreased for CdO thin film at wavelength in the range 580-750 nm.

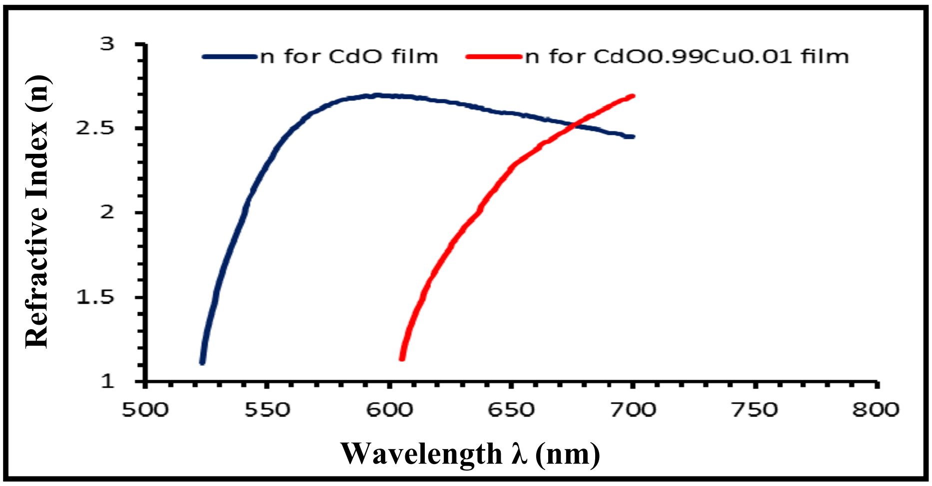

Fig.8: Refractive index as a function of wavelength of CdO and $CdO_{0.99}Cu_{0.01}$ thin films.

The relation between the extinction coefficient (k) and wavelength for CdO and $CdO_{0.99}Cu_{0.01}$ films deposited are shown in Fig.9. From this figure we can observe that k values of $CdO_{0.99}Cu_{0.01}$ film larger than k values of CdO film and take high values in the UV region, whereas it is decreasing in the visible region for CdO and $CdO_{0.99}Cu_{0.01}$thin films.

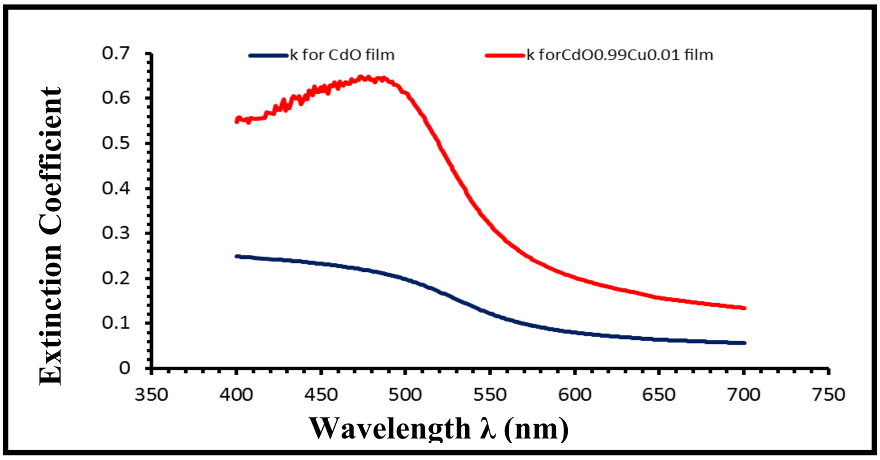

Fig.9: Extinction coefficient (k) as a function of wavelength for CdO and $CdO_{0.99}Cu_{0.01}$thin films.

The dielectric constant is defined as $\varepsilon(\omega)= \varepsilon_r(\omega) + i\varepsilon_i(\omega)$, real and imaginary parts of the dielectric constant are related to the n and k values. The ε_r and ε_i values were calculated using the formulas [15]:

$$\varepsilon_r= n^2 - k^2 \quad (3)$$

$$\varepsilon_i = 2nk \quad (3)$$

The variation of the real (ε_r) and imaginary (ε_i) parts of the dielectric constant values versus wavelength in the range 400-750 nm are shown in Fig. 10 a and b.

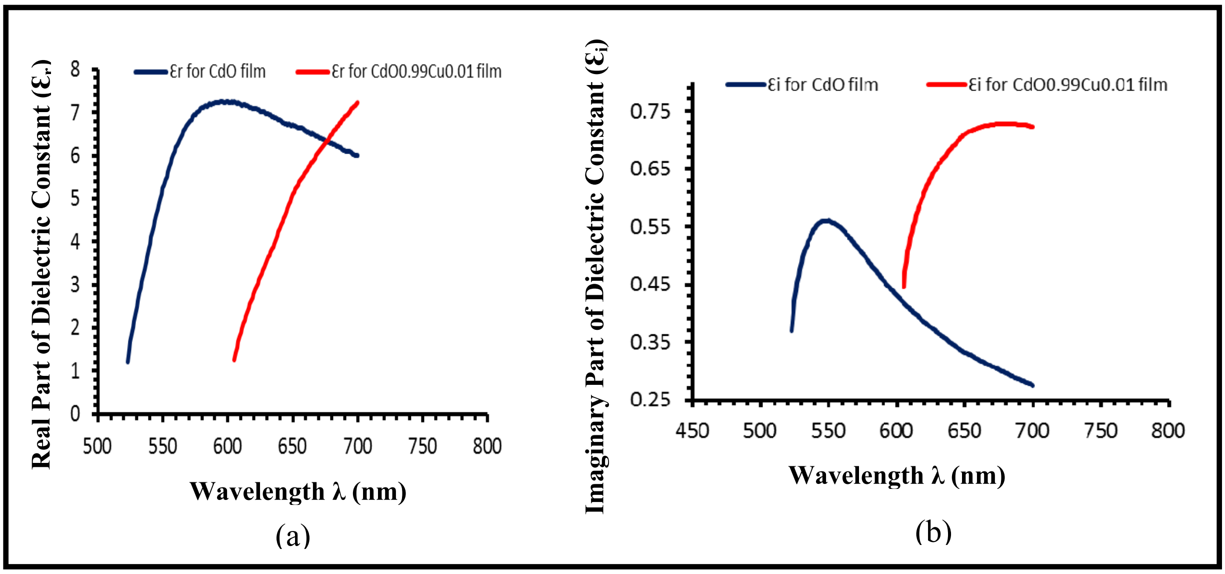

Fig. 10: Variation of dielectric constant parts (a) Real part (b) Imaginary part, for both CdO and $CdO_{0.99}Cu_{0.01}$ thin films.

From Fig. 10a it is clear that the real part of the dielectric constant for $CdO_{0.99}Cu_{0.01}$ thin film increase as the wavelength increase, while decreased for CdO thin film at wavelength in the range 590-750 nm. Also the variation of ($Ɛ_r$) has similar trend to the variation of the refractive index because of the smaller values of k^2 in comparison with n^2 and the values of real part are higher than imaginary part. Fig. 10b shows the imaginary part of the dielectric constant for CdO and $CdO_{0.99}Cu_{0.01}$thin films. The variation of the ($Ɛ_i$) mainly depends on the variation of k values which related to the variation of absorption coefficient. The imaginary part of dielectric constant for CdO thin film increase with wavelength but when reach 580 nm $Ɛ_i$ become decreases with increase the wavelength, while for $CdO_{0.99}Cu_{0.01}$ thin film this constant increasing with wavelength.

The Hall measurements show that the CdO and $CdO_{0.99}Cu_{0.01}$ films deposited on glass substrate are n-type semiconductor, the observed characteristics were supported from the measurements of mobility, conductivity, resistivity and Hall coefficient as illustrated in Table 2).

Table 2: Hall measurement for CdO and $CdO_{0.99}Cu_{0.01}$.

Parameter	CdO	$CdO_{0.99}Cu_{0.01}$
Bulk concentration ($1/cm^3$)	-2.208E+19	-5.202E+19
Mobility ($cm^2/V.s$)	3.995E+1	9.233E+1
Resistivity (Ω.cm)	7.076E-3	1.300E-3
Conductivity (1/ Ω.cm)	1.413E+2	7.6965E+2

The result shows the mobility and conductivity increase in $CdO_{0.99}Cu_{0.01}$thin films, where the resistivity decreases.

Conclusion

The CdO and $CdO_{0.99}Cu_{0.01}$ thin films prepared by pulse laser deposition technique were deposited on glass substrates. The thickness of the films was 500nm. The structure analysis shows that the films are polycrystalline structure. From UV-Visible transmittance, absorbance spectra, it observed that the optical transition in the CdO and

$CdO_{0.99}Cu_{0.01}$films to be direct transition. The energy band gap for CdO and $CdO_{0.99}Cu_{0.01}$ equals to 2.3eV and 2.2eV; respectively. The Hall measurements result show the films are n-type semiconductor and the mobility increase in $CdO_{0.99}Cu_{0.01}$films, while the resistivity decreases.

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