Effect of Annealing on the structural, surface morphology and optical properties for CdO:PbO composite thin films

Authors Names	ABSTRACT
<p>a. Rasha Hamid Ahmed b. Maad Mohammed Ameen</p> <p>Article History Received on: 10/5/2021 Revised on: 28 /5/2021 Accepted on: 31/5/2021</p> <p>Keywords: <i>Pulsed laser deposition, CdO:PbO composite, thin films</i></p> <p>DOI: https://doi.org/10.29350/jops.2021.26.3.1308</p>	<p>Thin films of pure cadmium oxide films (CdO) and composite with lead oxide (PbO) at different atomic ratios were prepared by pulsed laser deposition under vacuum using pulsed laser of ND-YAG from CdO and CdO:PbO targets. The prepared thin films were characterized by different technique before and after annealing at 500 °C. The X-ray diffraction shows polycrystalline structures of cubic CdO phase convert to sample of mixed phases for composites. The AFM images illustrate decreasing the particle diameter and increasing surface roughness with increasing the PbO ratio in composite. While, annealing cause to increase the particle size and reduce roughness. The optical absorbance increased with the PbO ratio, while the absorbance decreased with annealing. The energy gap reduced after annealing and increased with increasing the molar ratio of PbO. These variations in some fundamental properties of the prepared thin films by simply varying the components of the started target show the possibility of controlling the properties of the prepared thin films by pulsed laser deposition for use in many fields.</p>

1. Introduction

Thin film science is an important science that has many applications in several fields including optics, microelectronics, space sciences, medical sciences, etc. [6] Cadmium oxide (CdO) is a metallic oxide that is a direct bandgap semiconductor and is used by modern applications such as solar cells, gas sensors, and electronic circuits. CdO shows high conductivity at room temperature due to the high concentration of charge carriers[8]. Cadmium oxide has many advantages that can be controlled in a number of ways, such as deposition conditions and doping with other materials[4]. Recently, CdO films had been investigated using different deposition techniques such as SILAR method[4], sol-gel method [10] ultrasonic spray pyrolysis [13], pulsed-Laser deposition [1] etc. Doping is a very good way to manipulate the physical and chemical properties of semiconductors. [7]. CdO thin films properties, such as structural, optical

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and electrical properties, have been enhanced by different types of doping such as Mn doped CdO [10] Zn-doped CdO [3] Ce-Doped CdO [2] etc. Also, the annealing temperature is one of the important parameters, which optimize the structural, morphological, optical and electrical properties of CdO thin films. Numerous researchers investigated the effect of annealing temperature on these properties [5].

In this paper, we examine the effects of annealing temperature on the properties of CdO and CdO:PbO composite thin films, prepared by pulsed laser deposition, including structural properties, surface morphologies, and optical properties.

2. Experimental

CdO and $(\text{CdO})_{1-x}(\text{PbO})_x$ composite thin films were deposited on glass substrates by pulsed laser deposition technique from targets of mixed powders at different molar ratios ($x = 0.1, 0.2$ and 0.3). The targets were prepared by press using a hydraulic piston of the mixed powder as a pellet of 2 cm diameter into a stainless steel mould under the pressure of 5 tons for 15 min. Thin films were deposited on cleaned glass substrates inside a vacuumed chamber at 0.1 mbar pressure using Nd-Yag pulsed laser of 1064 nm wavelength (DIAMOND-288) of 300 mJ pulse energy, 10 ns pulse duration. The prepared thin films were characterized before and after annealing in the air for 1 h at 500 °C. The structural properties of thin films were examined using an XRD system (Shimadzu XRD 6000). Surface morphology was examined by atomic force microscope type (AA3000 Angstrom Advance Inc.). The UV-visible absorbance was measured by (SP-8001 spectrophotometer).

3. Results and Discussions

Fig. 1 shows the XRD for the $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films at different ratios prepared by the PLD technique on glass substrates after annealing. The prepared sample has good crystallinity as a result of annealing. The pure CdO sample has a pure cubic phase convert to mixed phases of CdO and Pb_3O_4 at a different percentage, in composite samples, according to the started materials ratio. The pure CdO sample has five diffraction peaks within the measurements located at $2\theta = 33.002^\circ, 38.293^\circ, 55.262^\circ, 65.892^\circ$, and 69.224° corresponding to the planes (111), (200), (220), (311), and (222) respectively identical with standard card No. 96-101-1004. Additional peaks appeared in the mixed samples corresponding to Pb_3O_4 identical with standard card No. 96-901-2703. The peak intensities for this phase increased with increasing the PbO ratio. From another side, the CdO peaks intensities decreased. The dominant phase at $x=0.3$ is the Pb_3O_4 though its lowest ratio indicates to high crystallinity of PbO crystals compared with CdO one. The preferred orientation for a pure sample is along (111) direction. These results agree with Gülenet *al*, [12]. There are shift in some peaks specially in sample $x=0.2$ and 0.3 due to strain in lattice as a result of lattice defects caused by doping.

Fig. 1: X-ray patterns for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films after annealing.

Fig. 2 shows the AFM images for the as deposited $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films prepared at different ratios and next to the associated particle size disruption. It seems from the figure and Table 1 that the average particles diameters were significantly decreased from 95.17 nm to 80.50 nm, while the roughness increased with increasing the PbO ratio due difference in growth mechanism [9].

Fig. 2: AFM images and cumulating distribution for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films before annealing.

Table 1: AFM parameters (Average Diameter, RMS roughness and Peak-peak distance) for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films before annealing.

Sample	Average Diameter (nm)	RMS roughness (nm)
CdO	95.17	4.3
0.1 PbO	91.24	4.8
0.2 PbO	90.61	5.2
0.3 PbO	80.50	6.3

Fig. 3 illustrates the AFM images and the cumulating distribution for particles diameters for the surface of $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films prepared at different ratios and annealed at 500 °C. Also, it appeared from the figure and Table 2 that the average diameter decreased, while the roughness increased with increasing the PbO ratio. The average diameter or samples after annealing larger than before annealing for all samples due to removing barriers between adjacent particle and

merge them making larger particles. While the roughness decreased after annealing and the particle destitution become narrower than that before annealing.

Fig. 3: AFM images and cumulating distribution for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films before annealing.

Table 2: AFM parameters (Average Diameter, RMS roughness and Peak-peak distance) for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films after annealing.

Sample	Average Diameter (nm)	RMS roughness (nm)
CdO	100.55	2.32
0.1 PbO	97.35	3.1
0.2 PbO	96.06	4.85
0.3 PbO	82.45	5.37

Fig. 4 shows the absorption patterns for the pure CdO samples and composite samples with PbO at different ratios. It seems that the absorption increase with increasing the PbO ratio, due to scattering for localized states created by doping. The absorption edge appeared at about 400 nm. The optical band gap E_g^{opt} was measured using the Tauc as shown in Fig. 5 was 3.85 eV for the sample without annealing.

Fig. 4: Absorption curves for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films before annealing.

Fig. 5: $(\alpha h\nu)^2$ vs. $h\nu$ for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films before annealing.

Fig. 6 shows the UV-visible absorption patterns for the $(\text{CdO})_{1-x}(\text{PbO})_x$ composite thin films at different ratios. Also, the absorption increased with increasing the PbO ratio. The annealing made the absorption edge sharper due to the reduction of the tail states of that located near the absorption edges, due to the reduction of crystal defects as a result of increased crystallization. The annealing also led to red shift in the absorption edge. The increase of the lead oxide ratio from 0 to 0.3 cause to increase in the optical energy gap from 2.5 to 2.6 eV, maybe due to the effect of the quantum confinement phenomenon due to the particle size reduced to the nanoscale range [11] as shown by the AFM tests.

Fig. 6: Absorption curves for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films after annealing.

Fig. 7: $(\alpha h\nu)^2$ vs. $h\nu$ for $(\text{CdO})_{1-x}(\text{PbO})_x$ thin films after annealing.

4. Conclusions

Pure CdO and CdO: PbO composite thin films at different atomic ratios were prepared by the PLD technique from target prepared from mixed powders. The X-ray diffraction shows polycrystalline structures of cubic CdO phase for a pure sample and mixed phases for doped ones. The AFM measurements show decreasing the average diameter and increasing roughness with increasing the PbO ratio. While annealing cause to increase the particle size, its distribution is narrower than before annealing and reduce roughness. Also, the optical properties are highly affected by adding PbO and by annealing, where the energy gap reduced after annealing and increased with increasing the molar ratio of PbO. These differences in the physical properties of the prepared thin films by varying the composite ratio by varying the ratio of the started target, show the viability of simply tuning the properties of the prepared thin films.

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