

Structural and Electrical Properties of Nanocrystalline CdO:In thin films Deposited by Pulsed Laser Deposition

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Abstract: The paper presents a review of indium-doped cadmium oxide (CdO:In) films were prepared by Pulsed Laser Deposition (PLD) on sapphire α -Al₂O₃ (006) and quartz substrates at different deposition condition by Nd-YAG Q-Switching second harmonic generation (SHG). The effect of doping on the structure and electrical properties of the CdO:In films have been investigated by X-Ray Diffraction (XRD). The result showed that nanocrystalline and (111)-oriented CdO films were obtained. The electrical hall effect properties include The conductivity , carrier concentration and Hall mobility show that n-type semiconductor films.. the D.C Conductivity shows that, one activation energy for all samples. The activation energy for pure CdO was (0.228 eV) for quartz and (0.234eV) for sapphire α -Al₂O₃ substrates and this value decreases to (0.515 eV) when the film doping at (3%) for quartz and (0.42eV) for sapphire α -Al₂O₃ substrates.

Key words: In doped CdO nanostructures, pulsed laser deposition, structure and electrical properties.

Introduction

Transparent conductive oxides (TCOs) are a type of non-stoichiometric semiconductor oxides of high conductivity arising from structural metal interstitials and oxygen vacancies. They have widespread use in many advanced technology applications. It is well known that high carrier mobility is essential for TCOs with good quality electro-optical properties. The TCOs have attracted much attention due to their importance in optical and electrical applications like in displays, gas sensors, solar cell technology [1, 2]. Cadmium oxide is a good transparent conductive material because their high transparency coefficient in visible region, high electrical conductivity and high optical transmittance in the visible region of solar spectrum along with a moderate refractive index make it useful for various applications, such as photodiodes, gas sensors,

etc. The CdO based materials could be widely used in high performance solar cells which contain a large amount of Cd [3,4]. It has n-type semiconducting property with a rock-salt crystal structure (FCC) and an optical band gap lies between 2.2-2.7 eV [5- 7]. The CdO semiconducting gas sensors is spreading more to detect the pollutants, toxic gases, alcohol and food freshness and used in moisture detectors, electronic sensors [8,9]. The morphology, the particle size and surface area are the important role in sensing materials. In the present work, CdO Nanocrystalline was synthesized via In doped CdO films were deposited on sapphire α - Al₂O₃ (006) and quartz substrate by pulse laser deposition technique, the structure and electrical properties were studied.

Experiment

CdO:In thin films were synthesized by pulsed laser deposition system using a second harmonic Nd:YAG laser. Thin films were grown in a vacuum chamber with background pressure of $\sim 1 \times 10^{-3}$ mbar. The Nd:YAG laser was operated at the wavelength of ($\lambda=533$ nm) with the repetition rate of (10Hz) and pulse duration of (7ns). The target to substrate distance was (3cm).

X-ray diffraction measurement has been done and compared with the JCPD cards, using Philips PW 1840 X-ray diffract meter of $\lambda = 1.54 \text{ \AA}$ from Cu-K α . The morphological features of the various films were investigated with a JEOL JSM-6360 equipped with a EDAX detector. The electrical measurements are achieved on prepared thin films including, D.C conductivity and Hall Effect. The resistivity of pure CdO and CdO:In films is measured by DC measurements after depositing metal electrodes (Al) on the samples using appropriate masks. The method comprises a temperature controller oven. The films glass samples

are heated in the oven from room temperature up to 300°C with step of 10°C. Electrical resistance is then measured directly for all steps with digital electrometer. The resistivity is conventionally calculated from measured electrical resistance. The activation energy is calculated from measuring the conductivity as a function of temperature using a cryostat, the temperature read out is by (MANFREDI L7C). The bias voltage was supplied by (FARNELL E 350) power supply. The current read out is by (*Kithley-616 Digital Electrometer*) multimeter.

Results and Discussion

The x-ray diffraction patterns of the prepared nanostructure CdO pure and CdO films of different doping concentrations (1, 3, 5 and 7%) on sapphire α -Al₂O₃(006) substrate are deposited by PLD technique analyzed by x-ray diffraction (XRD) as illustrated in figure (1). All the patterns show polycrystalline of cubic CdO structure (NaCl structure) and CdO:In films are composed of crystallites of CdO (JCPDS Card No:05-0640) [10]. The analyses evidence that most of the peaks belong to cadmium oxide with one peak back to Al₂O₃(006) substrate and one for CdO:In films. At the doping ratio (1, 3, 5 and 7%) become evident, indicating that it has formed a separate phase of Cadmium. Five diffraction peaks of CdO and one for CdO:In thin films appear at ($2\theta=33.86, 38.3, 55.35, 66.64$ and 69.35), which are corresponding to the (111), (200), (220), (311) and (222) planes of CdO, and ($2\theta=64.7$) which are corresponding to the (620) plane of CdO:In respectively. XRD shows neither the formation of CdO and In₂O₃ nor mixed phases even In-doping level. It can be clearly seen that all films are preferentially orientated along (111) crystallographic directions and this is in agreement with the result obtained by others on films prepared [11,12]. And the

preferential orientation peak for Indium doped films of different doping concentration became wide and less intense. Also observation of apparition of peak on doping films is orientated along (620) and increase with increasing of doping concentration.

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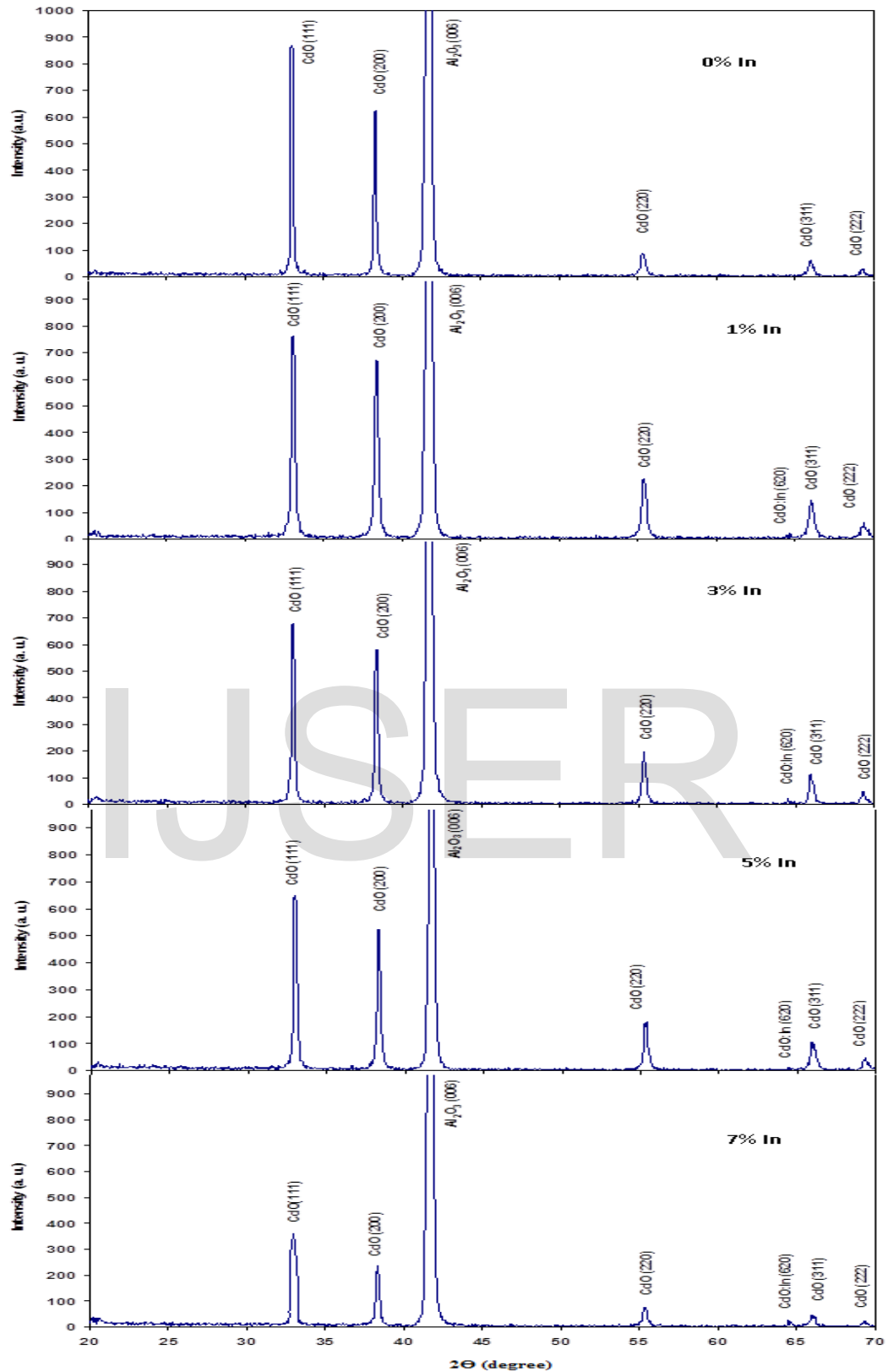


Figure 1: The X-Ray diffraction (XRD) patterns of the prepared CdO and CdO:In films of different doping concentrations.

The CdO film shows a preferential growth along (200) and (111) directions diffraction peak. However, the increase of indium concentration in the films induces the increase of (111) peak and decrease of (200) peak, as shown by the variation of diffraction intensity ratio of (111) to (200) with indium concentration in figure 2, which means the weakening of (200) preferential growth. Similar phenomena had been reported on the fluorine doping CdO film [10]. This phenomenon may be due to the presence of internal stress induced by the doping of indium during laser deposition, which can alter the energetic balance between different crystal planes orientations and lead to preferred texture in certain conditions [11]. The presence of indium in the CdO film may also change the diffusion rate of Cd and O at the surface during deposition, and hence lead to the variation of growth direction.

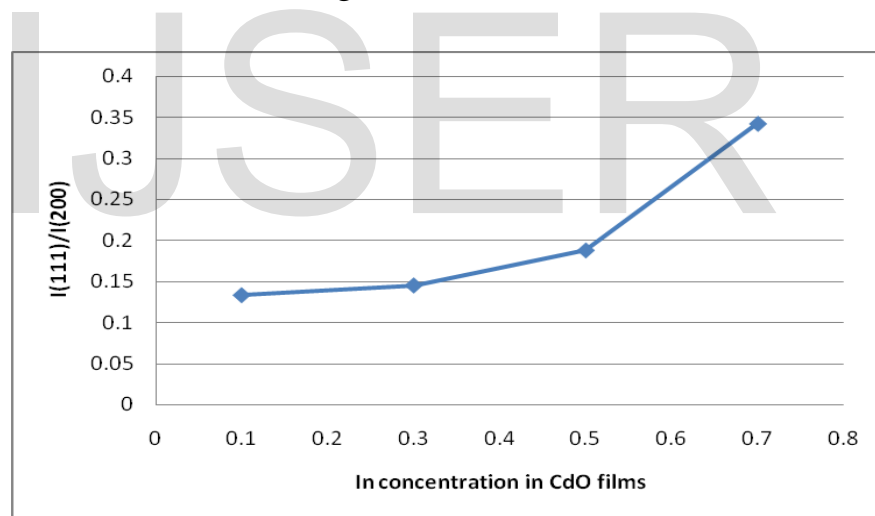


Figure 2 The variation of the integral intensity ratios of (111)/(200) with different In concentration .

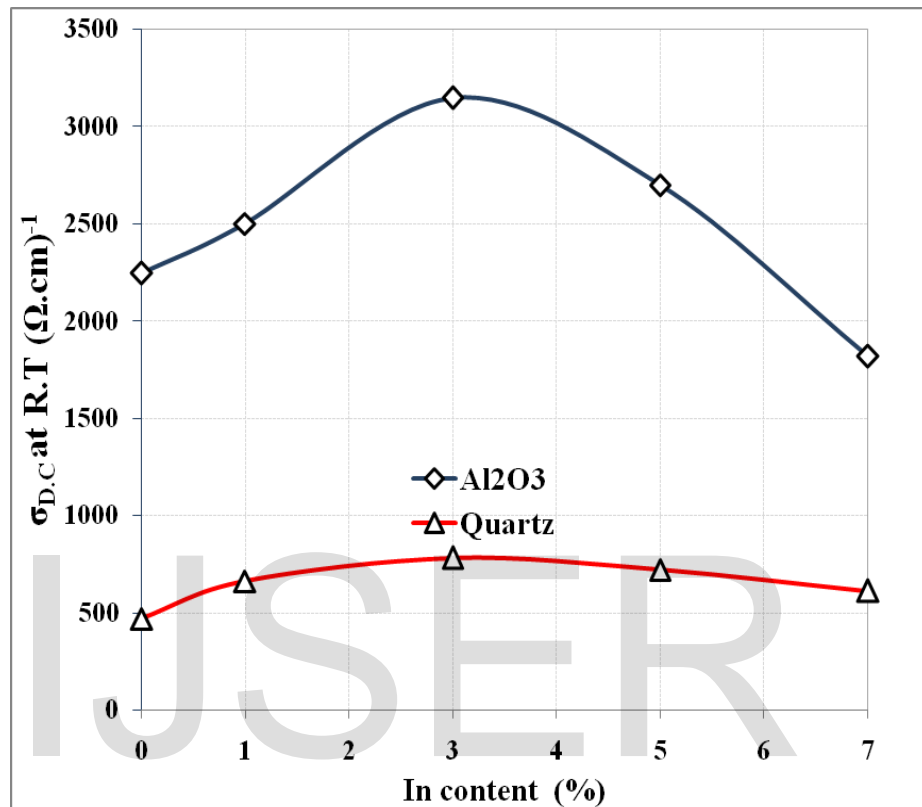
When the concentration of indium increases to 7%, the diffraction peak of In_2O_3 appears which implies that the maximum solid solution of indium element in CdO is less than 7%, locating at or exceeding this concentration, the film becomes a composite of CdO and In_2O_3 .

Electrical properties:

Hall Effect

The conductivity (σ), carrier concentration (n_H) and Hall mobility (μ_H) of the In-CdO films measured at room temperature, as a function of indium concentration in the films were shown in Figures. 3, 4 and 5.

Figure (3)
 Variation of



conductivity at RT ($\sigma_{D.C}$) with dopant ratio α -Al₂O₃ and Quartz substrates.

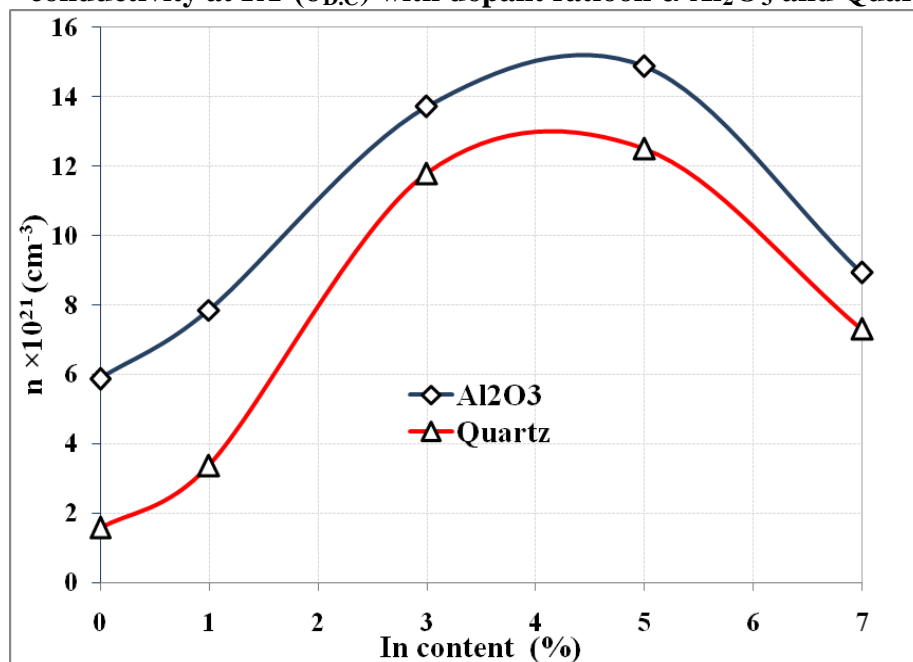


Figure (4) Variation of carrier concentration (n_H) with dopant ratio α -Al₂O₃ and Quartz substrates..

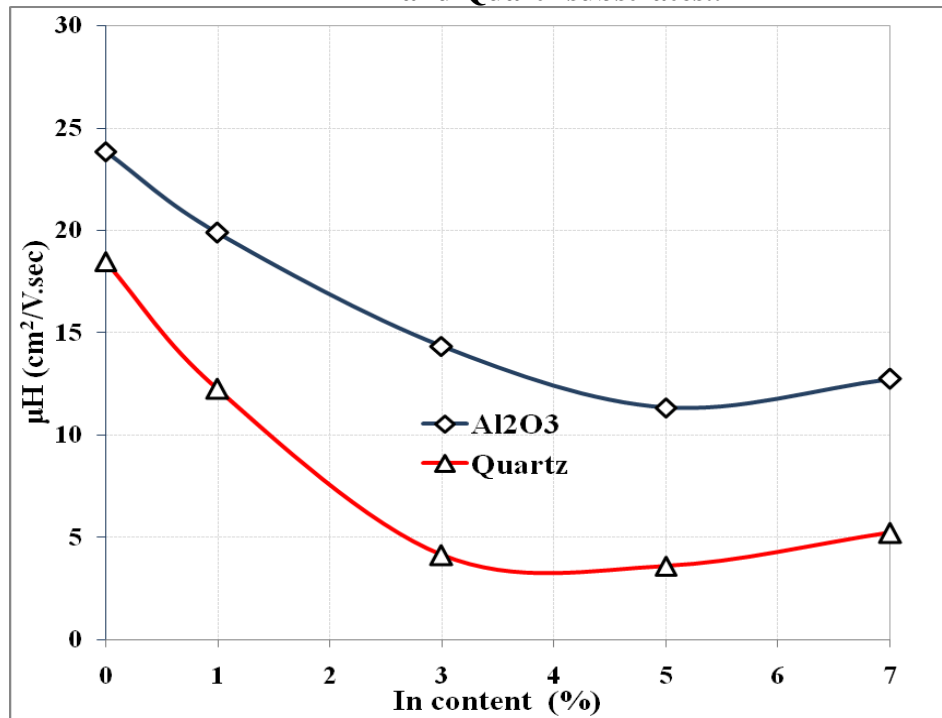


Figure (5) Variation of mobility (μ_H) with dopant ratio α -Al₂O₃ and Quartz substrates..

The conductivity of the deposited CdO films increases as indium concentration decreases to 3% and then decreases slightly as indium concentration increases further to 7%. While the carrier concentration increases obviously with increasing indium concentration to 5% and then decreases with further increasing indium concentration to 7%.

The electrical properties of the In-CdO films were comparing with other doped and undoped CdO films fabricated by different techniques. It is seen that the conductivity of 3% In-CdO film is $3148(\Omega\text{cm})^{-1}$, about twice of the value $2244(\Omega\text{cm})^{-1}$ of the undoped CdO films. This value is also much lower than the other metallic elements doped CdO films. The obtained electrical parameters and their variation can be explained by the doping concentration of indium and its existing state in CdO films. The dopant In ions in CdO film can either enter into the crystalline structure of CdO existing mainly in substitution a state or adsorb in grain boundary regions. Since In ions substituting Cd ions in Cd lattice can liberate more

conducting electrons in the conduction band, the increase of In concentration increase to certain concentration can significantly enhance the concentration of electrons and hence the carrier concentration [12].

CdO film. As a result, the resistivity was greatly decreased. However, as the indium concentration exceeds the solid solution limit of In ions substituting Cd ions in Cd lattice, superfluous In will exist as interstitial In or form In–O bonds like In_2O_3 , the latter was confirmed by the XRD patterns shown in figure 2; both of them tend to reside in or near grain boundaries. The increase of interstitial In ions (which act as donor centre) would result in remarkable enhancement of acceptor vacancies V^{2-}Cd in order to keep the charge balance in the crystal, which is responsible to the carrier concentration decrease. These non-conducting In_2O_3 clusters residing on CdO grain boundaries act as carrier traps rather than electron donors to decrease the carrier concentration in the films and hence increase the resistivity [13]. So, as the indium concentration increases to 7%, a decrease of carrier concentration and thus an increase of resistivity are observed. The conductivity, Hall coefficient, carrier concentration, and mobility for pure and doped CdO on Al_2O_3 and quartz substrate are shown in table 1.

Table (1) Hall measurements of CdO:In thin films prepared at different In dopant ratio on $\alpha\text{-Al}_2\text{O}_3$ and Quartz substrates.

μ_H ($\text{cm}^2/\text{V}\cdot\text{sec}$)	type	$n \times 10^{21}$ (cm^{-3})	$R_H \times 10^{-3}$ (cm^3/C)	σ_{RT} ($\Omega\cdot\text{cm}$) ⁻¹	In %	Substrate
24	n	5.88	10.60	2244	0	Sapphire $\alpha\text{-Al}_2\text{O}_3$
20	n	7.86	7.96	2500	1	
14	n	13.72	4.56	3148	3	
11	n	14.88	4.20	2700	5	
13	n	8.93	7.00	1820	7	
18	n	1.58	39.50	468	0	Quartz
12	n	3.38	18.50	661	1	
4	n	11.79	5.30	780	3	
4	n	12.50	5.00	720	5	
5	n	7.31	8.55	610	7	

D.C Conductivity

The electrical properties of the oxide semiconductors depend critically upon the oxidation state of the metal component (stoichiometry of the oxide) and on the nature and quantity of impurities incorporated in the films. Electrical conductivity (σ) depends on the concentration (N) and mobility (μ) of the relevant free carrier. Both high carrier concentration and mobility are required simultaneously to obtain films with high conductivity [14]. Also the electrical properties are strongly influenced by the morphology of the samples [15]. Doping with trivalent atoms creates more of the oxygen vacancies by substitution of the dopant on a Cadmium lattice site. This occurs because a +3 atom on a +2 site makes the Cadmium site feel a negative charge. D.C Conductivity increases with increasing doping percentage for (1%, 3%), and decreases in higher concentration (5%, 7%) as shown in table 2. The conductivity of undoped and doped CdO are due to the defects such as oxygen vacancies, lattice disorders, etc., which are results from incomplete oxidation of the films. Electrical conductivity is increase with concentration of oxygen vacancies [16]. The higher electrical conductivity for nanometric grains with low contribution of the grain boundary. In this case, the high (σ) is related to the homogeneous distribution of the carriers through the grain, differently from the non-nanosized grains in which the (σ) is associated to trapped carriers in the grain boundary [17]. The grain boundary effect has low contribution to the total conductivity and the main contribution for the electrical conductivity is due to the electron mobility inside the grain.

In low temperature region, the increase in conductivity is due to the mobility of charge carriers which is dependent on the defect/dislocation concentration. The conduction mechanism is usually called the region of

low temperature conduction. In this region activation energy increasing with increasing doping concentration for sapphire $\alpha\text{-Al}_2\text{O}_3$ substrate and have maximum value at 3% Indium doping for quartz substrate, because a small thermal energy is quite sufficient for the activation of the charge carriers to take part in conduction process. Hence increase in the conductivity in the lower temperature region can be attributed to the increase in charge mobility. In high temperature region, the activation energy is higher than that of low temperature region. In this region the electrical conductivity is mainly determined by the intrinsic defects and hence is called high temperature or intrinsic conduction. The variation of activation energy of the undoped and doped CdO films is summarized in Table 2.

Table 2: The Activation energy of different concentration of doped and undoped CdO for quartz and sapphire $\alpha\text{-Al}_2\text{O}_3$ substrates.

Activation energy (eV) sapphire $\alpha\text{-Al}_2\text{O}_3$ substrate	Activation energy (eV) quartz substrate	Doping Ratio
0.23419	0.22872	Pure
0.31947	0.31969	1%
0.37696	0.51542	3%
0.39467	0.33693	5%
0.4202	0.39059	7%

Conclusions

In this work, we have successfully prepared undoped and doped CdO with different concentration of In_2O_3 nanofilms on quartz and sapphire $\alpha\text{-Al}_2\text{O}_3$ substrates by Pulse laser deposition method. The

resulting films were characterized by XRD measurements. The diffraction pattern evidence that most of the peaks belong to Cadmium oxide with one of indium oxide peaks that appears at the higher doping ratio above 5%. The (111) and (200) is the dominant crystal structure that is the desired structure of CdO for sensing applications.

D.C Conductivity increases with increasing of doping percentage of (3%), and decreases for (pure, 1%, 5%, 7%) concentration, results show one activation energy for all samples. Hall measurements are showing that an increase of carrier concentration with increasing doping concentration, a high free carrier with doping of 3-5% indium oxide and then it decreases as the indium concentration increased. The semiconductors type Indium oxide reveals n-type semiconductor for all samples. The resistivity decreases at low doping and is increased at high level doping.

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