XRD Investigation of (PbO)$_{1-x}$(CdO)$_x$ Thin Films Deposited By Spray Pyrolysis Technique

Nahida Bukheet Hasan
Department of Physics, College of Science, University of Babylon
nahida1973@yahoo.com

Mohammed Ahmed
Department of Physics, College of Science, University of Babylon
iraq_mohiraq@yahoo.com

Abstract
Nano particles of Mixed (PbO)$_{1-x}$(CdO)$_x$ thin films were prepared by spray pyrolysis technique at a substrate temperature of 400°C. The films deposited were 160 nm thickness. The XRD analysis for its structural characteristic has been performed. The average grain size was found to be between 26 and 14 nm. Dislocation density, micro strain and layer number are found. It is understood that the crystallinity of PbO increases with increasing CdO Vol.%.

Keywords: Spray pyrolysis, Lead oxide, cadmium oxide , Structural properties , Thin films.

1. Introduction
Transparent conducting oxide (TCO) of thin films such as PbO, CdO, ZnO, SnO$_2$, In$_2$O$_3$ and MoO$_3$ have been studied in detail by many researchers [Cruz et al., 2005; Ferro et al., 2000]. These TCOs find extensive applications in thin film transistors, solar cells, phototransistors, optical storage devices, gas sensors, photo-thermal and photovoltaic conversions [Kumaravel et al., 2007]. Varieties of methods like dc reactive sputtering [Subramanyam et al., 2001], chemical bath deposition [Ocampo et al., 1994], activated reactive evaporation [K.T. Ramakrishna Reddy et al., 1998], solution growth [Verky and Fort, 1994], thermal oxidation [Ferrer, 1993], sol–gel [Galicia, 2000], and spray pyrolysis [B. Thangaraju et al., 2000] have been reported in the preparation of PbO and CdO thin films. The electro optical properties of CdO make this material very convenient as a solar cell material [Ferro et al., 2000]. Reportedly PbO exists in tetragonal (α-phase) and orthorhombic (β-phase) structures at low and high temperatures respectively [Baleva et al., 1994]. The difficulty of preparing exclusively single phase α- or β-PbO was pointed out earlier [Thangaraju et al., 2000 and Baleva et al., 1994]. The α-PbO was obtained earlier by pulsed laser ablation [Baleva et al., 1994] and spray pyrolysis [Thangaraju et al., 2000; Kirkbir et al., 1992]. The α-PbO was transformed to the meta-stable β-PbO when heat treated beyond 489 °C [Kirkbir et al., 1992]. In attempts to improvise the properties of PbO, it is being tried out to mix with other oxides. Recently, Hosono et al. [Trinquier and R. Hoffman, 1984] reported amorphous semiconductor 2CdO-PbO thin films with a novel information about the carrier generation through the formation of
oxygen vacancies. In the present work, we bring out a structural investigation on mixed (PbO)\(_{1-x}\)(CdO)\(_x\) thin films with 0≤x≤1 prepared from spray pyrolytic decomposition of aqueous solutions of lead and cadmium acetates at 400 °C.

2. Experimental work

2.1. Solutions Preparation:

PbO and CdO thin films were prepared by spraying an aqueous solution of Lead (II) acetate trihydrate and cadmium acetate. This solution was prepared by dissolving 3.973 gm of Pb(CH\(_3\)COO)\(_2\).3H\(_2\)O [which is a powder of white color, it's molecular weight (379.33 g/mol )] in 100 ml distilled water and 2.6653 gm of Cd(CH\(_3\)COO)\(_2\).2H\(_2\)O [which is a powder of white color, it's molecular weight (266.53 gm/mol)] in 100 ml distilled water too. The dissolving weight (W\(_t\)) of the materials [Pb(CH\(_3\)COO)\(_2\).3H\(_2\)O and Cd(CH\(_3\)COO)\(_2\).2H\(_2\)O] respectively were determined by using the following equation [R. Kumaravel et al. ,2007] :

\[ M = \frac{W_t}{M_{wt}} \times \frac{1000}{V} \]

Where:
M: is the molar concentration, equal {0.1M materials [Pb(CH\(_3\)COO)\(_2\).3H\(_2\)O and Cd(CH\(_3\)COO)\(_2\).2H\(_2\)O] }, M\(_{wt}\) : molecular weight, V : volume of distilled water.

The weights of [Pb(CH\(_3\)COO)\(_2\).3H\(_2\)O and Cd(CH\(_3\)COO)\(_2\).2H\(_2\)O] were measured by using electrical balance sensitive (Mettler. -160 ) four digits (10\(^{-4}\) g). Mixing the solutions with different Vol.% of (x) and leaving the solution for 24 hours to make sure that no residues were left and to ensure the homogeneity of the resultant solution. The resultant solution was sprayed on preheated glass substrates and silicon wafer to prepare (PbO)\(_{1-x}\)(CdO)\(_x\) thin films. When the solution is sprayed, the reaction takes place at the surface of the heated substrate, the equations (2) and (3) show the reaction. The resulting films were stable, whitish downhill to yellow in color, transparent, free from pinholes and have good adhesive properties.

\[
Pb(CH_3COO)_2 \cdot 3H_2O \rightarrow Pb(CH_3COO)_2 + 3H_2O \]

\[
Pb(CH_3COO)_2(s) \rightarrow PbO(s) + CH_3COCH_3(g) + CO_2(g) \]

\[
Cd(CH_3COO)_2 \cdot 2H_2O \rightarrow Cd(CH_3COO)_2 + 2H_2O \]

\[
Cd(CH_3COO)_2(s) \rightarrow CdO(s) + CH_3COOH(g) + CO_2(g) \]

2.2. The Parameters to Preparation Films

A simple homemade spray pyrolysis experimental setup was employed to prepare (PbO)\(_{1-x}\)(CdO)\(_x\) mixed thin films on glass substrates (35× 25×1.35 mm\(^3\)) at a substrate temperature of 400 °C. The difference in CdO vol.% (x) was achieved by mixing the aqueous solutions of 0.1 M of lead and cadmium acetates to pre-determined volume ratio. The value of (x) in the solution was varied from 0.00 to 1.00 (x=0, 0.2, 0.4, 0.6, 0.8, 1). The mixed solutions which were then diluted with water formed the final spray solution and a total volume of 25 ml was used in each deposition. The deposition parameters such as spray nozzle-substrate distance (30 cm), spray time (4 s) and the spray interval (1 min) were kept constant. The carrier gas (filtered compressed air) flow rate was
maintained at 6 l/min at a pressure of $6.5 \times 10^4$ Nm$^{-2}$. X-ray diffraction (XRD) analysis was used to recognize the crystal structure of (PbO)$_{1-x}$ (CdO)$_x$ thin films.

3. Results and Discussion

The X-ray Diffraction investigation has been carried out for the prepared mixed thin films of (PbO)$_{1-x}$ (CdO)$_x$ in Fig. (1), for range from 20°-70° in 2θ. According to (ASTM) cards, the structure of these films showed a polycrystalline. The XRD shows peaks whose position were shifted slightly from the data of (ASTM) card Increased by 0.03. The interplanner spacing ($d_{hkl}$) was determined using the Bragg relationship[S.M.Sze,1981] :

$$2d \sin \theta = n \lambda$$ .......................... (4)

Where $n$ is an integer that indicates the order of the reflection, $\theta$ is Bragg angle, and $\lambda$ is the wavelength of the X-ray beam. By measuring the Bragg angle $\theta$, the interplanar distance $d$ can be obtained if the wavelength of the X-ray beam is known [H. Hosono et al.,1996].

From Fig. (1.a) when $x = 0$ (PbO$_{\text{pure}}$) sample, three peaks which could be related to (101), (110), and (002) planes of the tetragonal $\alpha$-PbO phase were observed with cell parameters $a = b = 3.96$ Å and $c = 5.01$ Å. From Fig. (1.f) when $x = 1$ film (CdO$_{\text{pure}}$), the five diffraction peaks observed were identified as the reflections from (111)*, (200)*, (220)*, (311)* and (222)* planes of cubic CdO phase with a lattice parameter of 4.6948 Å [ICDD PDF file No:75-591]. The most prominent peak for the $x = 1$ was the reflection from the (111)* plane. The diffraction peaks corresponding to (111)* and (200)* planes were sharp in comparison to those from(220)*, (311)* and (222)* planes. The obtained reflections were consistent with the previous reports on CdO and (CdO)$_{1-x}$(PbO)$_x$ [8,19] films. It may be noted that Sarma and Srinivasan [19] reported five reflections for post-annealed (CdO) film with slight preferential direction along (111)* plane. It is palpable from Fig. 1 that the films in the present work which are not post-annealed show a strong preferential orientation along (200)*. The possible reason for the better crystallinity in the present study could be the difference in nozzle-substrate distance. The lesser distance of 30 cm in their study than that of 35 cm in the present study could possibly be influenced by the decomposition of the solvents, which in turn would have resulted in low crystallinity. The intensity of (101) and (110) reflections increasing with increase (CdO) vol.% (until $x = 0.6$) and then decreases slightly (at $x=0.8$ ), while the intensity of (002) reflection decreases with increasing (CdO) vol.% (at $x = 0.2$, 0.4 and 0.8 ) and increasing (at $x = 0.6$), Also we note that the intensity of (101) reflection (at $x=0.2$) be the prominent and controlling for other peak in (PbO) and (CdO) thin film , This refers to the clear improvement in the crystalline properties of the film, where it is known that (111) is the highest peak in intensity films (CdO) [8]. We also note that the phases of the films change with increasing (CdO) vol.% , Where they become orthorhombic $\alpha$-PbO phase with cell parameters, $a=5.6085$ Å, $b=5.6036$ Å and $c=4.9893$ Å. This is consistent with the researcher R. Kumaravel and et.al. [8]. As a result of this change in the phase films (PbO) has shown improvement in the crystal structure in terms of increasing intensity the reflection peaks and appearance of new peak (112) and (103), This refers to the improvement in the properties of the films.

For all films, the grain size (G.s) was calculated from the full width at half maximum (FWHM) ( $\beta$) of the preferred orientation diffraction peak by using the Debye-Shherrer's equation, eq.[Hosono et al.,1996]:
Where:

\[ D = \frac{0.9 \lambda}{\beta \cos \theta} \] 

... (5)

\( \lambda \): is the X-ray wavelength (Å), \( \beta \): FWHM (radian), \( \theta \): Bragg diffraction angle of the XRD peak (degree).

Larger G.s and smaller \( \beta \) values indicate better crystallization of the materials. According to Table (1). The (G.s) of (101) and (110) plane of PbO decreases from 24.57 nm and 44.59 nm respectively to 22.13 nm and 34.3 nm respectively on an increasing CdO vol.% (x) from 0.2 to 0.8. Whereas, the (G.s) of (002) plane increases from 11.25 nm to 25.01 nm for the increase in vol.% of (x). We also note the decrease in the average of grain size with increasing CdO vol.%; this shows an improvement in the structural properties of the prepared films.
Fig. (1): The X-ray diffraction patterns of the prepared films: a. PbO\textsubscript{pure}, b. PbO\textsubscript{0.8} CdO\textsubscript{0.2}, c. PbO\textsubscript{0.6} CdO\textsubscript{0.4}, d. PbO\textsubscript{0.4} CdO\textsubscript{0.6}, e. PbO\textsubscript{0.2} CdO\textsubscript{0.8}, f. CdO\textsubscript{pure}.
Table (1): X-ray diffraction data for (PbO)_{1-x} (CdO)_x for different Vol.% of (x).

<table>
<thead>
<tr>
<th>Sample</th>
<th>(hkl)</th>
<th>2Θ</th>
<th>Θ</th>
<th>d</th>
<th>FWHM</th>
<th>FWHM</th>
<th>G.S</th>
<th>Average G.S(nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PbO</td>
<td>(002)</td>
<td>35.42</td>
<td>17.71</td>
<td>0.253</td>
<td>0.740</td>
<td>0.01292</td>
<td>11.25</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111)*</td>
<td>33</td>
<td>16.5</td>
<td>0.271</td>
<td>0.277</td>
<td>4.847×10^{-3}</td>
<td>29.818</td>
<td></td>
</tr>
<tr>
<td>PbO_{0.8}CdO_{0.2}</td>
<td>(002)</td>
<td>35.55</td>
<td>17.775</td>
<td>0.252</td>
<td>0.6481</td>
<td>0.011311</td>
<td>12.867</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(311)*</td>
<td>65.85</td>
<td>32.925</td>
<td>0.1447</td>
<td>0.555</td>
<td>9.695×10^{-3}</td>
<td>16.881</td>
<td></td>
</tr>
<tr>
<td>PbO_{0.6}CdO_{0.4}</td>
<td>(101)</td>
<td>28.51</td>
<td>14.255</td>
<td>0.3127</td>
<td>0.3703</td>
<td>6.463×10^{-3}</td>
<td>22.130</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(111)*</td>
<td>32.95</td>
<td>16.475</td>
<td>0.2715</td>
<td>0.5740</td>
<td>8.079×10^{-3}</td>
<td>17.802</td>
<td></td>
</tr>
<tr>
<td>PbO_{0.4}CdO_{0.6}</td>
<td>(002)</td>
<td>35.48</td>
<td>17.74</td>
<td>0.2527</td>
<td>0.3333</td>
<td>5.817×10^{-3}</td>
<td>25.014</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(200)*</td>
<td>38.28</td>
<td>19.14</td>
<td>0.2348</td>
<td>0.4814</td>
<td>8.402×10^{-3}</td>
<td>17.459</td>
<td></td>
</tr>
<tr>
<td>PbO_{0.2}CdO_{0.8}</td>
<td>(002)</td>
<td>35.70</td>
<td>17.85</td>
<td>0.2512</td>
<td>0.555</td>
<td>9.695×10^{-3}</td>
<td>15.018</td>
<td></td>
</tr>
<tr>
<td></td>
<td>(220)*</td>
<td>55.29</td>
<td>27.645</td>
<td>0.1663</td>
<td>0.9444</td>
<td>9.049×10^{-3}</td>
<td>16.795</td>
<td></td>
</tr>
<tr>
<td>CdO pure</td>
<td>(111)*</td>
<td>32.95</td>
<td>16.475</td>
<td>0.2715</td>
<td>0.37</td>
<td>4.847×10^{-3}</td>
<td>9.476</td>
<td></td>
</tr>
</tbody>
</table>

Note: 2Θ and Θ values are given in degrees (deg), d values in nm, FWHM values in degrees (deg), FWHM values in radians (rad), G.S values in nm, and Average G.S(nm) values in nm.

Additionally, to have more information on the amount of defects in the films, number of layers \( (N_l) \), micro strain \( (\varepsilon) \) and the dislocation density \( (\delta) \), were evaluated in table (2) from equations (6), (7) and (8) respectively [Illican et al., 2008].

\[
N_l = \frac{t}{D^3} \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \qu
4. Conclusion

The XRD studies confirmed the orthorhombic $\alpha$-PbO phase and cubic CdO phase. Further, it is understood that the crystallinity of PbO increases with increasing CdO vol.%. The calculated mean crystallite size of the selected planes of PbO and CdO were found varying between 26 and 14 nm. The variation of crystallite size corroborates with XRD patterns.

5. References