Influence of deposition temperature on the properties of spray pyrolysed CdO thin films for TCO application

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Abstract

Transparent and conducting cadmium oxide (CdO) thin films were deposited onto soda-lime glass substrate by simple chemical spray pyrolysis technique at different deposition temperatures. The influence of the deposition temperature on structural, morphological, electrical and optical properties of CdO films was investigated. X-ray diffraction patterns revealed that polycrystalline CdO phase with cubic crystal structure started to form at deposition temperature of 300 °C with secondary phase, while at lower deposition temperature the prepared layers showed amorphous structure. At deposition temperature higher than 300 °C, the prepared layers showed single CdO phase enhanced crystallinity. Enhanced grain growth of CdO films is observed with increasing the deposition temperature. Moreover, the electrical conductivity of the films was found to be increasing with increasing the deposition temperature, which is consistent with the enhanced grain growth. Additionally, the optical transmittance measurement of the CdO films showed around 90% transmission in the visible and near infrared regions, independently of deposition temperature.

Keywords: Transparent conducting oxides; CdO; spray pyrolysis; deposition temperature, and grain growth.

1. Introduction

Among these techniques, chemical spray pyrolysis technique is simple, cost effective and suitable for large area preparation.

In the present study, CdO thin films were deposited by chemical spray pyrolysis technique at different deposition temperatures between 200 and 450 °C using compressed air as carrier gas. The prepared films were characterized to study the influences of deposition temperature on their structural, morphological, electrical and optical properties.

2. Experimental

The CdO films were deposited onto soda-lime glass (SLG) substrates by spray pyrolysis technique. An aqueous solution of 0.1 M cadmium acetate((CH₃COO)₂Cd·2H₂O) were dissolved in a distilled water. The desired chemical reaction is following:

\[\text{Cd(CH}_3\text{COO)}_2\cdot 2\text{H}_2\text{O} \rightarrow \Delta \rightarrow \text{Cd(CH}_3\text{COO)}_2 + 2\text{H}_2\text{O}\] (1)

\[\text{Cd(CH}_3\text{COO)}_2(s) \rightarrow \Delta \rightarrow \text{CdO(s)}+\text{CH}_3\text{COCH}_3(g) + \text{CO}_2(g)\] (2)

The deposition parameters such as spray nozzle–substrate distance (25 cm, solution rate(0.66 (ml/min)) and pressure of carrier gas(25 (L/min)) were optimized. The solution was sprayed onto preheated SLG at deposition temperatures of 200, 300, 350, 400 and 450 °C. X-ray diffraction (XRD) patterns of prepared films were obtained by Philips diffractometer model (PW3040) using Kα₁ radiation (λ=1.54 Å). The morphology of the films was studied by Scan Electronic Microscope FEI Quantum model (FEG 250). The thickness of the prepared films were measured using a Stylus profilometer model (Dektak 150). The optical transmittance (T) and reflectance (R) were obtained by UV/Vis/NIR spectrophotometer model (Jasco-670) in the wavelength range 200–2500 nm.

3. Results and discussion

3.1. Structural properties

Fig.1(a,b,c,d) shows X-ray diffraction patterns for the samples deposited at deposition temperatures of 300, 350, 400, 450°C respectively. X-Ray diffraction patterns of the deposited films showed that CdO phase begin to form at 300 °C, where the deposited films at 200°C were amorphous. The deposited films at 200 °C were amorphous as the temperature is not enough to form CdO phase, while at 300 °C the peaks of CdO begin to appear with an unidentified phase where the temperature is not sufficient for the complete evaporation and decomposition of the starting precursors. However, by further increase in the deposition temperature, the secondary phase disappeared and CdO reflections became stronger and sharper as the crystallinity started to enhance with further increase in the deposition temperature. The observed CdO reflections were indexed according to the cubic structure (JCPDS no. 05-0640) showing reflections corresponding to(111),(200), (220),(311) and (222) planes.
The average crystal grain size ($D$) was estimated using Scherrer's formula [B.D. Cullity, 1956]:

$$D = \frac{0.94\lambda}{\beta\cos\theta} \quad (3)$$

where $\theta$ is the usual Bragg angle and $\beta$ is the full width at half-maxima of the diffraction peaks.

The structural parameters for (1 1 1) crystallographic orientation of the CdO thin films shows that with increasing the deposition temperature from 300 °C to 450 °C, the crystallite size increases from 10.8nm to 24nm, indicating improvement in the crystallinity of the films with increasing the deposition temperature.

3.2. Morphological properties
SEM is a convenient technique to study the surface morphology of thin films. Fig. 2a,b,c and d show the SEM images of the CdO thin films deposited at deposition temperatures of 300, 350, 400 and 450 °C respectively. The surface property of the CdO films appears to change as a function of deposition temperature. The grain growth of CdO was found to be enhanced with increasing deposition temperature as shown in Fig. 2. With increasing the deposition temperature, the small clusters are merged with each other to form bigger grains and the CdO films become more compact, dense and adhered to the entire substrate without any cracks.

![SEM images of CdO thin films sprayed at 300, 350, 400 and 450 °C](image)

**3.3. Electrical properties**

The electrical conductivity of CdO thin films prepared at different deposition temperature was measured using two-probes configuration. Fig. 3 shows the variation of electrical conductivity with deposition temperature. The electrical conductivity increased with increasing deposition temperature, which may be attributed to the enhanced crystallinity and grain growth of the films with increasing the deposition temperature.

![Conductivity of CdO thin film deposited at different deposition temperatures for 15 min.](image)
3.4. Optical properties

The optical transmittance spectra for the CdO thin films prepared at different temperatures are shown in Fig. 4. All prepared films show high transparency in both visible and near IR regions. It can be seen that by increasing the deposition temperature, the transparency increases. This increase in transparency can be attributed to a decrease in thin film thickness, where the thickness of the film prepared at 300, 350, 400, 450 °C are 410, 310, 167 and 162 nm respectively. At 450°C the prepared CdO thin film shows higher transmission which reaches up to 90%.

![Fig. 4. Influence of different Tsub on the optical transmission spectrum of CdO](image)

The $E_g$ value can be calculated using the fundamental absorption, which corresponds to electron excitation from the valance band to conduction band. $E_g$ is usually obtained by extrapolations of the linear portion of the plots of $(\alpha h\nu)^2$ vs. $h\nu$, as shown in Fig. 5, where $h\nu$ is photon energy and $\alpha$ is the absorption coefficient expressed as:

$$\alpha = \frac{\ln(T)}{d} \quad (4)$$

where $T$ is transmittance and $d$ is film thickness.

![Fig(5) Relation between (ahu)² and hυ for CdO thin films prepared at different temperature](image)
The relation between the absorption coefficient and the incident photon energy \((\alpha h\nu)\) is given by the equation (6)

\[(\alpha h\nu)^2 = A(h\nu - E_g) \quad (5)\]

where ‘A’ is a constant and ‘E_g’ is optical band gap.

The value of direct energy band gap \(E_g\) is about 2.3 eV which is in agreement with the literature [A.J. Varkey, 1993] & [I. Ben Miled, 2017].

From Fig(5) it can be seen that there are two energy bands for films prepared at 300 and 350 °C confirming that there are two phases in the prepared films. For films prepared at 400 and 450 °C there is just one energy band gap indicating one phase in CdO films.

4. Conclusion

Highly conducting and transparent CdO thin films were successfully deposited on soda lime glass substrate by spray pyrolysis technique. The influence of the deposition temperature on structural, morphological, electrical and optical properties of CdO films was investigated. X-ray diffraction patterns revealed that polycrystalline CdO phase with cubic crystal structure begin to form at deposition temperature of 300 °C. The film grown at deposition temperature 450 °C show high crystallinity, high transmittance up to 90% in the visible and near infrared regions, low resistivity (86.8 \(\times 10^{-4}\) Ωcm). These highly conducting and transparent CdO thin films could be an excellent candidate for future optoelectronic applications.

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5. References

تأثير درجة حرارة الترسيب على خصائص الأغشية الرقيقة من أكسيد الكادميوم المحضر بطريقة الانحلال الحراري للريذان

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تم تحضير أغشية رقيقة من أكسيد الكادميوم بطريقة الانحلال الحراري بالرذاذ ودراسة تأثير درجات حرارة الترسيب المختلفة على الخواص الفيزيائية للعينات المحضرة واظهرت النتائج أن الكسيد الكادميوم بدأ في التكون عند درجة حرارة 333 درجة سيلزيوس وان نسبة التبلور للعينات تزداد مع زيادة درجة الحرارة وكذلك وجد ان الخواص الضوئية والكهربيه تتحسن مع زيادة درجة الحرارة حيث وجد ان العينات المحضره عند اعلي درجة حراره تم التحضير عددها وهي 453 درجة سيلزيوسي تتمتع باعلي نسبة تبلور واعلي توصيله كهربائي وكذلك اعلي شفافيه للضوء سواء في النطاق الضوئي او نطاق الاشعة تحت الحمراء.