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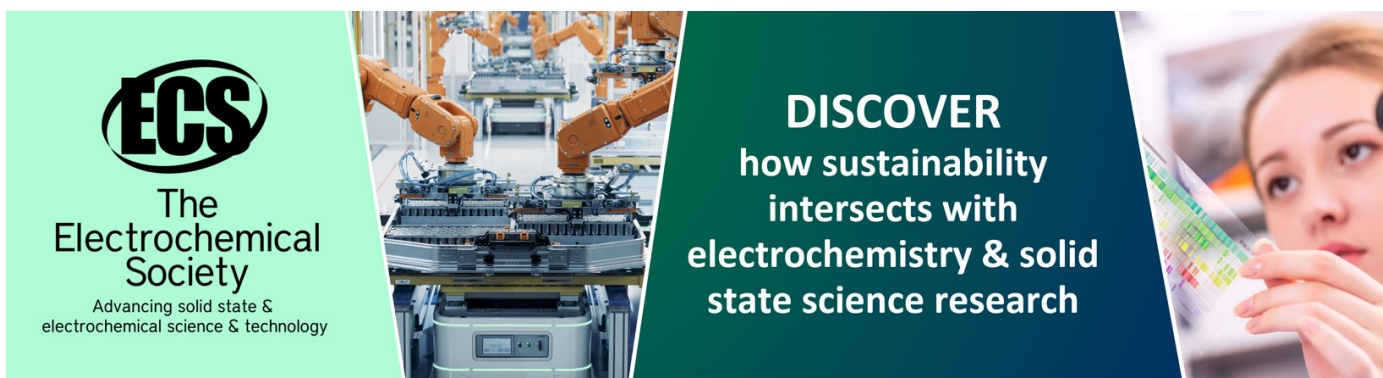
Microstructure and electric properties of spray pyrolyzed CdO thin films grown on SILAR deposited CdO seed

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Microstructure and electric properties of spray pyrolyzed CdO thin films grown on SILAR deposited CdO seed

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Abstract. In this report, a substantial effect of seed layer on structural and electrical properties of CdO thin film have been presented. Thin films of CdO have been synthesized by spray pyrolysis method at 400 °C on seed layer of CdO grown by SILAR method on glass substrate at 85 °C. XRD study revealed a mono-phasic cubic structure of CdO thin films oriented along (2 0 0) plane with highest intensity when grown on seed layer. Electrical conductivity, Hall mobility, carrier concentration are found substantially high using seed layer which suggests that seed layer plays a crucial role to enhance better physical and electric properties of CdO films.

1. Introduction

There is an ever growing interest in the synthesis of low-cost, transparent conducting oxides (TCOs) with n-type conductivity [1]. CdO is an n-type semiconductor having band gap between 2.2 and 2.7 eV [2] and shows low resistivity due to defects of oxygen vacancies and cadmium interstitials [3]. In search of such suitable TCOs, it is found that chemical and physical conditions can be conveniently incorporated in the CdO thin films to obtain higher transmission and conductivity [1]. Cadmium oxide (CdO) thin films are regarded as a material with as large energy band gap, high optical transparency in the visible spectral region, remarkable luminescence characteristics etc. Due to these properties, CdO is a promising material for electronic or optoelectronic application, such as solar cells application, photodiodes and gas sensors [4]. For the increase of solar cell efficiency it is necessary to reduce energy loss in electrodes. Therefore, resistivity of electrodes should be as low as possible. In a good crystalline film, it is expected, defect will minimum and thereby carrier scattering will also be minimum. As a result, resistivity will be low in a good crystalline film. For obtaining low resistive and good crystalline film, crystalline seed layer was used on glass substrate for preparation of CdO film.

Up to now, various techniques such as sputtering [5, 6], vacuum thermal evaporation [7] pulsed laser deposition (PLD) [8], chemical vapor deposition (CVD) [9], successive ionic layer adsorption and reaction (SILAR) [10, 11], sol-gel [12,13], spray-pyrolysis (SP) [14], chemical bath (CB) [15] and so on are employed to grow CdO thin films. Among these, spray pyrolysis technique is simple, safe and low-cost, but effectively capable of producing film of high aspect ratio with desired crystalline quality. Moreover, in SP method excellent control of chemical uniformity, stoichiometry in multi-component system and varying band gap materials processing are possible in air ambient [16-19].

In this work, we present a new approach, a combination of spray and spray on seed layer (seed prepared by SILAR technique) method called 'spray on seed layer growth' to fabricate CdO thin films.



First, a very thin layer (seed layer) of CdO on glass substrate was deposited by SILAR technique and then spray was made on the seed layer from the solution of $(\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O}$ at 400°C . As-grown films were studied to observe the effect of seed layer on the structure and electric properties of CdO thin films.

2. Experimental

A very thin seed layer of CdO has been deposited on glass substrate by SILAR method, over which CdO thin films have been prepared by spray pyrolysis method at 400°C . For this purpose cadmium acetate di-hydrate $((\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O})$ (Merck 99.9%) was used as precursor for Cd^{2+} ion source and H_2O_2 for anion source.

For obtaining a good seed layer of CdO on glass substrate by SILAR method it is necessary to clean substrate properly, otherwise adhesion of seed on glass would be poor. As a result seed layer will be washed out during spray. The following protocol was adopted for substrate cleaning.

- i) Glass substrates were dipped into detergent about 24 hours, cleaned thoroughly in a stream of cold water and then washed by the de-ionized distilled water.
- ii) The substrates were then dipped into nitric acid for 1 hour and then washed thoroughly in distilled water and then dried.
- iii) These substrates were then dipped into piranha solution (solution of H_2SO_4 and 30% H_2O_2 in a proportion of 1:3) for one hour and then held in a stream of cold water for some times followed by rinsing with de-ionized distilled water several times. Finally, they were dried by blowing hot air with the help of drier and preserved in a slide holder for use.

a) Preparation of seed layer: CdO seed layer was prepared by a four-step SILAR technique using a solution comprising 0.1 M cadmium acetate $((\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O})$, 25% ammonia solution with a pH value 11.5 at room temperature. Hydrogen peroxide (H_2O_2) solution was used as the source of anion. For CdO seed preparation, following four steps were adopted:

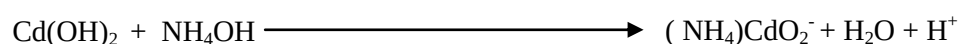
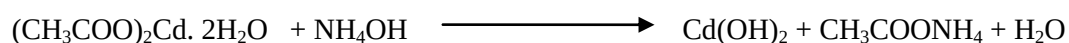
STEP-1: At first 0.1 M cadmium acetate $((\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O})$ was taken in a beaker and ammonia solution (25%) was instantly poured into it. The pH value of this solution was fixed at 11.5. The well-cleaned substrates were inserted into this solution for 30 seconds so that the Cd^{2+} ion adhered onto the glass substrate and form a very thin layer of $\text{Cd}(\text{OH})_2$, shown in figure 1(a).

STEP-2: This $\text{Cd}(\text{OH})_2$ layer was washed with distilled water in order to remove loosely bound cationic particles. Then the substrates were dipped into warm distilled water $((85 \pm 5)^\circ\text{C})$ about 10 to 15 seconds, shown in figure 1(b).

STEP-3: Immediately after step-2, substrates were dipped into a cationic source hydrogen peroxide (H_2O_2) solution (0.05M) for 30 seconds for anion uptake on the substrate. The complex layer deposited on the substrate during the dipping in hydrogen peroxide (H_2O_2) bath will be decomposed to CdO, shown in figure 1(c)].

STEP-4: Finally, the substrate was dipped into hot water $(85 \pm 5)^\circ\text{C}$ for 10 to 15 seconds followed by withdrawal of substrate and dried. These four steps together with complete a full cycle, as shown in figure 1(d)].

The possible chemical reactions that take place on the glass substrate at different stages during formation of CdO seed are given below:



b) Spray on seed: In spray pyrolysis, condensation of atoms or molecule onto a heated substrate forms a thin film of CdO. Spray deposited film was formed using 0.01M cadmium acetate $[(\text{CH}_3\text{COO})_2\text{Cd} \cdot 2\text{H}_2\text{O}]$ by conventional spray technique [20]. For obtaining a good quality film, optimized growth conditions were nozzle to substrate distance 21 cm, spray rate 0.3 ml/min, spray time 20 min. and substrate temperature 400 °C.

The chemical reaction that takes place on the heated substrate in spray method is given as:

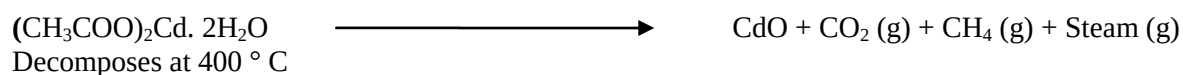


Figure 1. Schematic representation of SILAR method (a) cationic precursor and (c) anionic precursor and (b, d) de-ionized water.

An X-Ray diffractometer (D2 PHASER BRUKER) was used to study the structural properties of CdO films deposited on glass substrate by SILAR, spray and spray on seed layer growth techniques. The X-ray diffraction of all samples has been recorded within Bragg angle (2θ) of 20 ° to 70 ° using monochromatic $\text{CuK}\alpha$ radiation of wavelength $\lambda = 0.1542$ nm, from a source power 30 kV-10 mA. Temperature dependent electrical conductivity and RT Hall voltage measurements were performed by Vander Pauw's method using Keithley electrometer (England). Substrate temperature was controlled directly by adjusting voltages in a digital multi-meter (KT105) Temperature was monitored by a copper-constantan thermocouple. For Hall field, an electromagnetic type magnetometer (Newport instruments Ltd. England) was used at constant magnetic field of 0.9815 Tesla. Thicknesses of the films were (180 ± 10) nm measured by Newton's ring method.

3. Result and discussion

3.1 Structural Properties

The physical properties of thin films are highly related to their structure. A typical XRD pattern of CdO thin films prepared by SILAR, spray and spray on seed layer growth are shown in figure 1. In this figure, the presence of several peaks in the XRD patterns reveal that all the films are polycrystalline and characteristic reflection peaks are assigned to the (111), (200), (220), (311) planes by comparing with the standard, JCPDS card No. 75-0594 [21]. From XRD patterns, it is seen that films are polycrystalline in nature and have cubic CdO single phase. The highest intensity peak of CdO was produced by SILAR technique in (111) plane but for spray and spray on seed layer growth techniques, it was in (200) plane. It has also been observed that CdO film on seed layer showed highest intensity of reflections in (200) plane. The highest peak intensity and sharpness of the peak indicate better crystallinity of the films. The film grown on glass substrate by SILAR technique has

[111] preferred orientation, which is energetically favorable for CdO observed by other methods too, but for spray and spray on seed growth, preferred orientation changed to [200]. This change of orientation indicates that growth of CdO film at high temperature is energetically favorable in [200]. It seems the microstructure of CdO lattice changes due to growth on seed layer which inevitably perturbed the lattice thermodynamic energy of the growth planes, thereby, at high temperature growth of CdO on seed layer [200] plane is energetically more favorable.

The crystallite size (ζ) was estimated by using the Debye-Scherrer formula [22],

$$\zeta = \frac{K \lambda}{\beta \cos \theta} \quad (1)$$

where, K is a constant close to unity (0.94). The parameter λ is the wavelength of the X-ray used, θ is the diffraction angle and β is the full width at half maxima (FWHM) measured in radians. The dislocation density (δ), defined as the dislocation lines per unit volume of the crystal, has been calculated by using the formula [23],

$$\delta = \frac{1}{\zeta^2} \quad (2)$$

The lattice strain (η) is calculated using the relation [23], $\eta = \frac{\beta}{4 \tan \theta}$ and the estimated values are presented in Table 1.

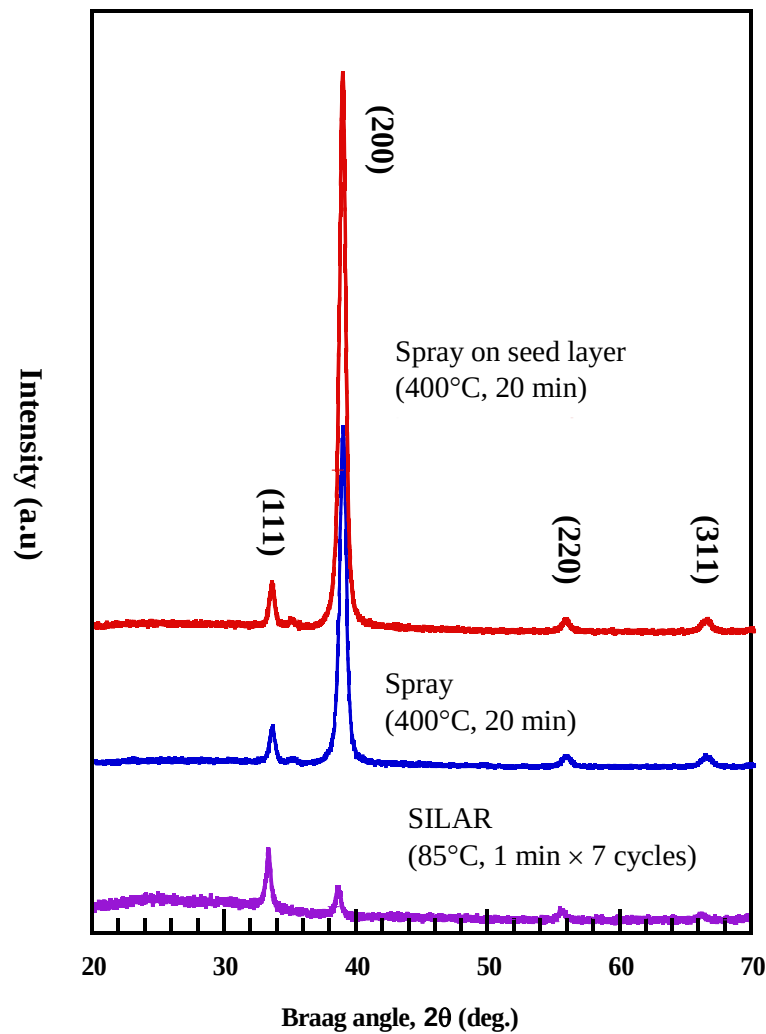


Figure 2. XRD pattern of CdO thin films

Table 1. Estimated lattice parameter, crystallite size, strain and dislocation density of CdO thin film for (200) plane.

Deposition method	Lattice parameter, a (nm)	Crystallite size, ξ (nm)	Lattice strain, $\eta \times 10^{-3}$	Dislocation density, $\delta \times 10^{-3} \text{ (nm)}^{-2}$
SILAR	0.4660	34	1.95	0.32
spray	0.4573	24	4.79	1.99
spray on seed	0.4634	23	4.38	1.62

3.2 Electrical Properties

The Vander Pauw's electrical conductivity with temperature for CdO film is shown in figure 3. There is a small upturn of conductivity from 300 K to 330 K noticeable for sprayed film, which is ascertained as poor metallic nature [20] of CdO film due to degeneracy, after which normal semiconducting behaviour was observed. On the other hand, spray on seed thin film shows semiconducting behaviour all through the measured temperature range. However, both films show very high conductivity but spray on seed film shows about four time higher conductivity compared to sprayed film which would make spray on seed film more efficient as solar cell electrode.

Hall voltage measurement at room temperature results n-type carrier concentration of the order of $\sim 10^{20}/\text{cm}^3$ but the pre-exponential term is more than four times higher for spray on seed layer growth compared to spray growth alone. However, mobility almost same but substantially higher compared to other growth methods, and also the carrier concentration and RT conductivity are much higher than other studies as presented in Table 2 for comparison. All these transport parameters of this study show superior to other growth technique [2, 9, 24], which are costly and need vacuum environment.

The activation energy of CdO thin film was estimated from the relation,

$$\sigma = \sigma_0 \exp(-\Delta E/2k_B T) \quad (3)$$

where ΔE is the activation energy, k_B is the Boltzmann constant and σ_0 is the pre-exponential term. Inset of figure 3 shows the plot of $\ln \sigma$ vs. $1000/T$ for CdO thin films fabricated by spray and spray on seed layer growth methods. The slope of the curves gives the activation energy. Activation energy for sprayed film is 0.043 eV and 0.003 eV for spray on seed film. These activation energy values suggest electrical transport is thermally governed in CdO thin film.

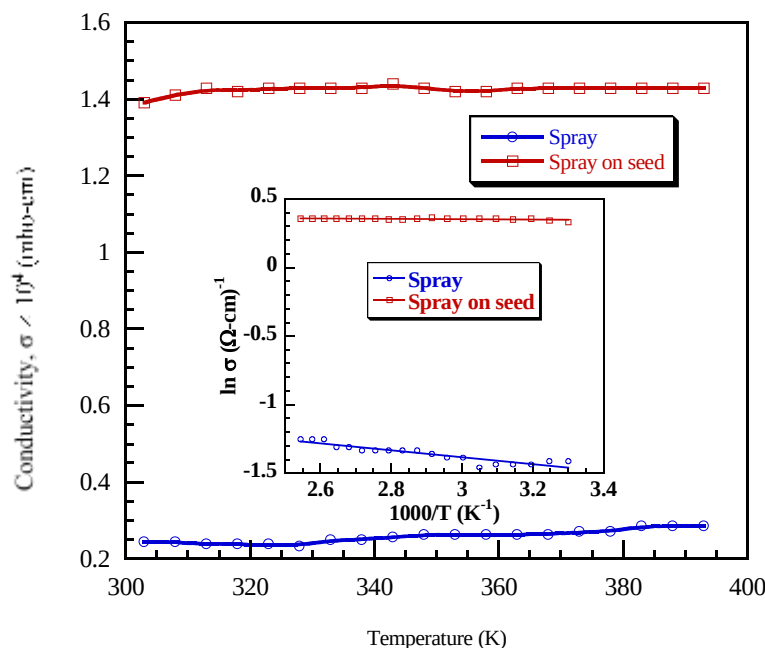
**Figure 3.** Variation of electrical conductivity with temperature and $\ln \sigma$ versus $1000/T$ (inset) graph

Table 2. Hall mobility, carrier concentration, RT conductivity and activation energy of CdO thin film.

Deposition method	Hall mobility μ_H (cm ² /V-sec)	Carrier concentration $\times 10^{20}$ (cm) ⁻³	RT Conductivity $\sigma \times 10^4$ (mho-cm)	Activation energy, ΔE (eV)	Ref.
Spray	33	4.5	0.24	0.043	this work
Spray on seed	34	20.4	1.11	0.003	this work
MOCVD	32	0.24	0.026	-	[9]
SGDC	8.0	0.39	0.005	-	[24]
TE	7.03	4.43	0.005	-	[2]

4. Conclusions

Spray and spray on seed layer growth CdO thin films were prepared to observe the effect of seed layer on the physical properties of CdO films and the following conclusions are made:

- CdO thin films prepared by spray and spray on seed layer are mono-phasic having cubic rock salt structure; preferred orientation [111] for seed layer grown by SILAR technique changed to [200] when CdO sprayed on seed at high temperature. Spray on seed layer growth technique provide structurally better film over spray method because of CdO seed layer on glass substrate acts as a building block for crystallization.
- Very high RT conductivity, $\sigma = 1.1 \times 10^4$ (mho-cm), high mobility, $\mu_H = 34$ (cm²/V-sec) and high carrier concentration, $n = 20.4 \times 10^{20}$ (cm)⁻³ were obtained for CdO film prepared by spray on seed growth technique. High values of these transport properties suggest CdO film prepared by spray on seed layer would be more efficient for solar cell electrode and opto-electric device applications.
- Activation energy values suggest electrical transport is thermally activated in CdO film.

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References

- [1] Yusuf G T, Babatola B K and Ishola A D 2016 *Science and Engineering Applications* **1**(7) 92-95
- [2] Dakhel A A 2008 *Semicond. Sci. Tech.* **23** 055017
- [3] Zhao Z, Morel D L and Ferekides C S 2002 *Thin Solid Films* **413**, 203
- [4] Naser G Y, Raja W N, Faris A S, Rahemd Z J, Salihe M A and Ahmed A H 2013 *Energy Procedia* **36** 42- 49
- [5] Zhou Q, Ji Z, Hu B, Chen C, Zhao L and Wang C 2007 *Mater. Lett.* **61** 531
- [6] Saha B, Thapa R and Chattopadhyay K K 2008 *Sol. Energy Mater., Sol. Cells* **92**, 1077
- [7] Suhail M H, Ibrahim I M and Mohan Rao G 2012 *J. Electron. Dev.* **13** 965
- [8] Yan M, Lane M, Kannewurf C R and Chang R P H 2009 *Appl. Phys. Lett.* **78** 2342
- [9] Lamb D and Irvine S J C 2009 *Thin Solid Films* **518** 1222
- [10] Salunkhe R R and Lokhande C D 2008 *Sens. Actuators* **B129**, 345
- [11] Ergin B, Ketenci E and Atay F 2009 *Int. J. Hydrogen Energy* **34** 5249
- [12] Ayala A M, Delgado G T, Perez R C and Angel O Z 2010 *J. Alloys Compd.* **506** 554

- [13] Ilıcan S, Caglar M, Caglar Y and Yakuphanoglu F 2009 *Optoelectron. Adv. Mater. Rapid Commun.* **3** 135
- [14] Jeyaprakash B G, Kesavan K, Kumar R A, Mohan S and Amalarani A 2010 *J. Am. Sci.* **6** 75
- [15] Al-Ogılı H K J 2011 *Eng. Technol. J.* **29** 1536
- [16] Rao T P, Kumar M C S, Angayarkanni S A and Ashok M 2009 *Journal of Alloys and Compounds* **485** 413
- [17] Babu B J, Maldonado A, Velumani S and R Asomoza 2010 *Materials Science and Engineering* **B174** 31
- [18] Manouni A E et al. 2006 *Superlattices and Microstructures* **39** 185
- [19] Rahman M Met al. 2012 *Journal of Materials Science & Technology* **28** 329
- [20] Khan M K R, Rahman M A, Shahjahan M, Rahman M M, Hakim M A, Saha D K and Khan J U 2010 *Curr. Appl. Phys.* **10** 790-796
- [21] Usharani K and Balu A R 2015 *Journal of Acta Metall. Sin., Engl.* **28(1)** 64-71
- [22] Cullity B D 2001 *Elements of X-ray diffraction*, Prentices Hall, New Jersey **388** 619
- [23] Yilmaz M, Aydin S, Turgut G, Dilber R and Ertugrul M 2012 *Progresses in Nanotechnology and Nanomaterials* **1(1)** 5-8
- [24] Murali K R, Kalaivanan A, Perumal S and Pillai N N 2010 *J. Alloys Compd.* **503** 350-353