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Structural, optical and electrical properties of chemically sprayed CdO thin films

C.H. Bhosale *, A.V. Kambale, A.V. Kokate, K.Y. Rajpure

Electrochemical Materials Laboratory, Department of Physics, Shivaji University, Kolhapur 416 004, India

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Abstract

The cadmium oxide (CdO) thin films have been deposited onto amorphous and fluorine doped tin oxide (FTO) glass substrates using spray pyrolysis technique. The aqueous solution containing precursor of Cd has been used to obtain good quality deposits at optimized preparative parameters. The films have been characterized by techniques such as X-ray diffraction (XRD), optical absorption, electrical resistivity and thermoelectric power (TEP) measurements. The XRD study reveals that the films are polycrystalline with cubic structure. Optical absorption studies reveal that the value of absorption coefficient is in the order of 10^4 cm^{-1}, indicating direct band to band transition with band gap energy 2.26 eV, close to its value of intrinsic band gap energy. The electrical characterization shows that the electrical resistivity (ρ) is of the order 10^{-3} Ω cm and it decreases with increase in temperature indicate the samples are semiconducting in nature. The value of activation energy is found to be 0.077 eV. TEP measurement shows the thermoelectric voltage for CdO films is positive towards the hot end, indicating n-type behavior of sample. The value of TEP increases with increase in temperature. The Hall effect measurement study reveals that the carrier concentration (n), Hall coefficients (R_H) and carrier mobility (μ_H) are of the order of 10^{23} cm^{-3}, 10^{-8} cm^3/C and 10^{-4} cm^{-2}/V s, respectively.

Keywords: Spray pyrolysis; Thin films; CdO; XRD; Optical absorption; Electrical resistivity; Hall coefficient and mobility

1. Introduction

The studies on semiconducting thin film are being pursued with increasing interest on account of their proven and potential applications in many semiconductor devices such as solar energy converters, optoelectronic devices [1–6]. The first report of a transparent conducting oxide (TCO) was published in 1907, when Badeker reported that thin films of Cd metal deposited in a glow discharge chamber could be oxidized to become transparent while remaining electrically conducting. Since then, the commercial value of these thin films has been recognized, and the list of potential TCO materials has expanded to include, for example, Al-doped ZnO, GdInOx, SnO_2, F-doped In_2O_3, and many others [7].

TCOs are essential part of technologies that require both large-area electrical contact and optical access in the visible portion of the light spectrum. High transparency, combined with useful electrical conductivity ($>10^3$ Ω^{-1} cm^{-1}), is achieved by selecting a wide-band gap oxide. The CdO compound being one of the TCOs, is reddish brown in color and is formed by burning of Cd in air. The oxide is insoluble in water, absorbs CO_2 from air and can be reduced to the conducting oxides have received very little attention; though it is one of the promising candidate for optoelectronic field [8–10]. The CdO have special features such as high conductivity, high transmission, and low band gap made it applicable in photodiodes, phototransistors, photovoltaics, transparent electrodes, liquid crystal displays, IR detectors and antireflecting coatings [9–11]. Preparation of semiconducting CdO thin films by magnetron dc sputtering and spray pyrolysis on Si and glass substrates have reported for their surface, structural and photoluminescence studies [12–15].

Amongst all the deposition techniques spray pyrolysis is simple, quick, economical and suitable method for large area deposition for many binary and ternary semiconducting thin films. The growth can easily be controlled by preparative

* Corresponding author. Tel.: +91 2312690571; fax: +91 2312691533.
E-mail address: bhosale_ch@yahoo.com (C.H. Bhosale).

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parameters such as spray rate, substrate temperature, concentration of solution, nozzle frequency, etc. [16,17].

The present study deals with the preparation of CdO thin films onto preheated amorphous and FTO-coated glass substrates by the spray pyrolysis technique. The films have been characterized by different techniques such as X-ray diffraction (XRD), optical absorption, electrical resistivity, thermoelectric power (TEP), and Hall effect for further investigation, which is essential to make full use of their active properties.

2. Experimental

The thin films of CdO were deposited onto preheated amorphous and fluorine doped tin oxide (FTO)-coated glass substrates at temperature 400° C by spraying 50 cm^3 aqueous solution of 0.1 M cadmium acetate [Cd $(CH_3COO)_2$]. The nozzle to substrate distance was kept fixed at 30 cm and spray nozzle was moved back and forth over the substrates with a frequency of 0.26 cycles/min. During the deposition the spray rate was kept constant to be 4 cm^3/min. When the droplets of sprayed solution reach the hot substrate, owing to the pyrolytic decomposition of solution, well adherent, pinhole free, uniform yellowish colored films of cadmium oxide were formed on the surface of substrates.

The structural characterization of the thin film was carried out by analyzing the XRD pattern obtained using a Philips X-ray diffractometer model PW 1710 (λ = 1.5405 Å for Cu Kα). The XRD patterns obtained for the films grown on bare micro slides glass plates were scanned in 2θ range of 10–100°.

The thickness of the film was measured by weight difference method assuming the films are uniform and dense as that of bulk having density of 8.15 g/cm^3.

The optical absorption studies were carried out in the wavelength range 350–850 nm by UV–vis–IR spectrophotometer Hitachi (Japan) model 330.

The electrical resistivity (ρ) of the films was studied by two-probe method in the temperature range 300–500 K. The TEP measurement was carried out in the temperature range 300–550 K with the help of thermoelectric power unit, which consists of a brass, which gives the uniform temperature gradient along the length of the sample.

The electrical parameters such as electrical resistivity (ρ), carrier concentration (n) and Hall mobility (μ_H) at room temperature were measured by Hall effect set up supplied by scientific instruments Roorkee. Van der Pauw's technique [18] was used to measure these parameters. Specially designed Hall probe on printed circuit board was used to fix the sample of size 1 cm × 1 cm.

3. Results and discussion

In the Spray pyrolysis method, starting materials required to form the desired semiconducting compound are in the form of solutions, which are sprayed onto preheated substrates, resulting in the formation of thin films on the upper surface of the substrate. When the droplets of the above-sprayed solution reach to the hot substrate, owing to pyrolytic decomposition of the solution, well adherent, pinhole free uniform yellowish colored films of CdO are formed at substrate temperature of 400 °C. The possible chemical reaction that takes place is as follows:

$$Cd(CH_3COO)_2 + 3H_2O \xrightarrow{\text{Heat}} CdO\downarrow + CH_4\uparrow + 4H_2\uparrow + 3CO_2\uparrow$$

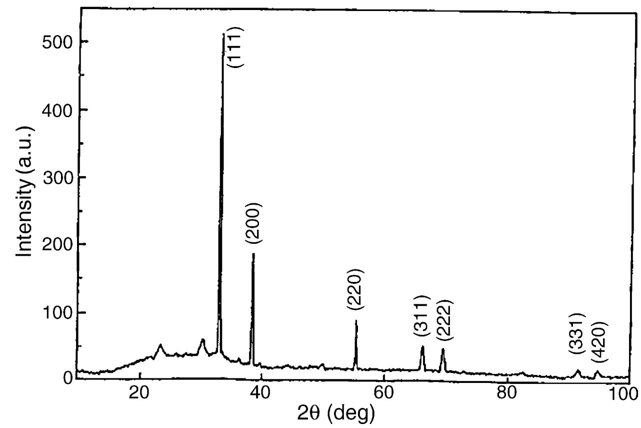

Fig. 1. The XRD pattern for CdO thin film deposited at substrate temperature of 400 °C and solution concentration of 0.1 M.

The XRD pattern obtained for the film grown on bare microslides glass plate was studied in 2θ range of 10–100° and is shown in Fig. 1 which indicates that the sample is polycrystalline in nature. It also indicates the presence of (1 1 1), (2 0 0), (2 2 0), (3 3 1), (2 2 2), (3 3 1) and (4 2 0) planes for cubic CdO. Table 1 compares the calculated d values of CdO with the standard ones [19]. A matching of the observed and the standard d values confirms that the deposited film is of CdO having cubic crystal structure. The lattice parameter a is calculated for cubic structure of CdO film. The calculations lead to a = 4.66 Å.

The optical absorption of the film was studied in the wavelength range 350–850 nm. The variation of optical density with wavelength is further analyzed to find out the nature of transition involved and the optical band gap. The nature of

Table 1
Comparison of observed and standard 'd' values for CdO thin film deposited at 400 °C substrate temperature

Sr. no.	Standard 'd' values (Å)	Observed 'd' values (Å)	($h\,k\,l$) Plane
1	2.71	2.70	(1 1 1)
2	2.34	2.34	(2 0 0)
3	1.65	1.65	(2 2 0)
4	1.41	1.41	(3 1 1)
5	1.35	1.35	(2 2 2)
6	1.07	1.07	(3 3 1)
7	1.04	1.04	(4 2 0)