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# Radio frequency power induced changes of structural, morphological, optical and electrical properties of sputtered cadmium oxide thin films

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ABSTRACT

Transparent and conducting cadmium oxide (CdO) thin films were deposited on glass substrates at room temperature using radio frequency (RF) magnetron sputtering method. The carrier concentration and electron mobility are the key factors for the conducting properties of CdO thin films. The grain size, crystallinity, thickness, surface roughness and band gap of CdO thin films play an important role in optical and electrical properties. In this study, dual behaviour of CdO thin films is studied as a function of RF sputtering power. Crystalline quality, micro structure, surface morphology and optical and electrical properties of sputtered CdO thin films were investigated. The structural analysis revealed that the deposited CdO films were polycrystalline in nature with cubic structure ($Fm\bar{3}m$ space group). The grain sizes were found to be increased with increase of RF power from 100 to 150 W and then decreased at high power (200 W). The optical studies revealed that all the films exhibited higher transmittance in visible and near infrared region and the optical energy band gap value decreased from 2.62 to 2.46 eV with increase of RF power. Luminescence spectra exhibited two strong emission peaks at 484 and 519 nm. The resistivity of CdO thin films gradually decreased with an increase of sputtering power and reached a minimum value of $3.041 \times 10^{-4}\,\Omega$ cm at 200 W. A maximum mobility of 67.01 $cm^2/Vs$ was found for the sample prepared at the sputtering power of 150 W.

## 1. Introduction

Transparent conducting oxide (TCO) materials possess unique combination of low resistivity and high optical transparency within the visible region of the electromagnetic spectrum. Recently, TCO materials have received considerable attention and are rapidly developed due to higher performance, good fabrication process and low cost for their wide range of applications in optoelectronic circuits and interfaces [1]. Despite the properties of these materials, stagnation of the combination of high transparency and conductivity of the films is a major problem. Recently, several significant research works have been carried out to improve the properties of TCO such as carrier concentration, electron mobility and optical transparency by choosing suitable method of deposition [2], optimizing the deposition conditions [3], using pre and post thermal treatment [4], substrate variations [5], doping compounds [6] and so on. Pure and doped tin oxide ($SnO_2$), indium oxide ($In_2O_3$), cadmium oxide (CdO), zinc oxide (ZnO), gallium oxide ($Ga_2O_3$) are the well-known binary TCO materials. Among the post-transition metal oxides, CdO is the third member of the series followed by $SnO_2$ and $In_2O_3$ and it is one of the most significant representatives of n-type degenerate TCO material [7]. In the last few years, CdO has received great attention of the scientific perspectives as one of the promising semiconducting materials for its excellent properties such as cubic structure, high thermal stability, strong ionic character, excellent surface activity, high optical transmission (70–98%) in the visible and near infrared regions, low optical direct band gap (2.2–2.5 eV), moderate refractive index, remarkable luminescence characteristics, high electrical conductivity ($10^{-4}\,\Omega$ cm) even without doping, high carrier concentration ($1 \times 10^{19}-1 \times 10^{21}$ $cm^{-3}$) and high electron mobility which make it useful for countless applications such as conducting electrode [8], antireflection coating [9], Photo diode [10], Photo transistor [11], liquid crystal display [12], smart window [13], optical wave guides, Infrared detector [14], solar cell [15] and gas sensor [16] etc. In CdO thin films preparation, several methods have been used such as RF/Direct current (DC) magnetron sputtering [17], thermal evaporation [18], Pulsed Laser deposition [19], chemical bath deposition

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[20], spray pyrolysis [21], and spin coating [22], etc. When RF sputtering technique is compared with the above mentioned methods, it has better film adherence, uniform deposition over the large area of various substrates, control over the contaminants, high stability and deposition rate, small substrate temperature rise during film deposition etc. Thus, it can be commonly used in semiconducting industry to deposit various thin films for IC processing [23], fabrication of CDs and DVDs, antireflection coating etc. The physical properties of CdO thin films prepared from RF sputtering technique strongly depend on deposition parameters such as sputtering (RF) power, substrate temperature, deposition time, vacuum condition, substrate to target distance, sputtering gas (Argon) pressure and nature of the substrate [24,25]. The sputtering RF power is one of the important parameters which plays a vital role on the thickness, structural, morphological and optoelectronic properties of various types of thin films. However, several studies on the effect of RF power on the physical properties of thin films have been reported and available in the literature [26–30]. A profound understanding of the fundamental aspects of transparent semiconductors is therefore required to improve either the properties of existing materials, or design new type of TCOs. In the present work, nano-crystalline CdO thin films are deposited by RF magnetron sputtering technique by varying the sputtering RF power and keeping other sputtering parameters as constant. The present work deals with elaborative discussion of the effect of RF power on thickness, micro structure, morphological, compositional, optical and electrical properties of CdO thin films. The results of crystallite size, optical band gap, resistivity and conductivity of CdO thin films with respect to the RF power have also been reported here.

## 2. Experimental procedure

### 2.1. Target preparation and film deposition

CdO thin films were deposited on microscopy glass substrates (26 mm × 76 mm, 1.2 mm thickness) by RF magnetron sputtering technique (HINDHIVAC; Planar Magnetron RF\DC Sputtering System Model-1200 MSPT) in an argon atmosphere at room temperature using stoichiometric pure CdO target. The CdO target was prepared by using commercially available CdO powder with high purity (99.999%) purchased from Merck limited (India) as a source material. The CdO powder was preheated at 800 °C for eight hours in an ambient atmosphere to reduce the shrinkage stress. The preheated CdO powder was mixed with poly vinyl alcohol (PVA) used as a binder and continuously ground for 10 h in order to obtain homogeneous mixture. Then, it was compacted into a pellet of size 5 cm diameter and 5 mm thickness with the help of stainless steel pelletizer and hydraulic press. Finally, the pellet was sintered at 700 °C for seven hours in box furnace in order to improve the hardening and ductility with greater resistant to cracking which could be used as a target material for RF sputtering system. The prepared CdO target was loaded into circular planar cathode portion inside a stainless steel covered chamber. The chamber was evacuated to higher vacuum degree of the order of $2 \times 10^{-3}$ Pa using rotary and diffusion pumps. Later, the pure argon gas was introduced into the chamber with the flow rate of 25 sccm. These yielded a pressure of $3 \times 10^{-1}$ Pa in the chamber during deposition. Before deposition, the substrates were subjected to etching and cleaning processes using chromic acid solution and acetone. After cleaning, the substrates (anode) were fixed perpendicular to the cathode surface at a distance of 6 cm from the target. Initially, the pre sputtering process was carried out for 5 min with a view to remove any organic and inorganic residuals on the surface of the target and to reach the equilibrium condition, the Radio Frequency (RF) power was adjusted from 100 W to 200 W and the deposition was carried out for 30 min.

### 2.2. Characterization

The thickness of CdO thin films were measured using a stylus profilometer (Mitutoya SJ-301) equipped with diamond needle. The crystalline structure and texture of the films were analyzed by X ray diffraction (XRD) measurements (XPERT-PRO PAN analytical) using the source of $CuK\alpha_1$ at the wavelength of 0.154 nm and the pattern was taken in the range of $2\theta = 20^\circ - 80^\circ$. The X-ray source was operated at a voltage of 40 kV, current 30 mA and the scanning step size of 0.05°. The surface morphology of CdO thin films were examined by field emission scanning electron microscope (FESEM) (VEGA3TE SCAN) operating at 30 kV. The compositions of the films were identified by energy dispersive spectroscopy (EDS) (BRUKER) using silicon drift detectors (Apollo X). The electron beam has diameter in the range of 1 nm to 1 μm, operated at a voltage of 30 kV and the spectrum was taken in the counting time of 10 ns with two different spots. The optical properties of the films were studied by using UV Vis-NIR spectrophotometer (JASCO, V670) in the wavelength range of 400–1000 nm. The luminescence properties were analyzed by using Varian Cary Elipse spectrophotometer using Xenon Lamp as a source with excitation wavelength 380 nm. The electrical properties such as resistivity, conductivity, carrier concentration and mobility were studied by Hall measurements (Ecopia-HMS 3000) with a magnetic field of 0.57 Tesla in Van der Pauw configuration at room temperature.

## 3. Results and discussion

### 3.1. Film thickness analysis

Film thickness plays a crucial role in microstructral, morphological, optical and electrical properties of CdO thin films. In RF sputtering technique, thickness of the films not only depends on the sputtering yield but also depends on the formation of negative ions, production of secondary electrons and their energies. In the present study, thicknesses of CdO thin films were found in the range of 850, 960 and 480 nm for 100, 150 and 200 W respectively. Sputtering (RF) power has direct influence on film thickness and deposition rate. When RF power was increased to 150 W, thickness of the film was increased. Upon further increasing the power to 200 W, thickness of the film was found decreased. At low sputtering power, minimum number of positive ions ($Ar^+$) was produced which ejected minimum number of atoms and this yielded lower growth rate as well as minimum thickness of the film. On increasing RF power, more number of argon atoms was ionized which promoted large number of atoms ejected from the target. In addition, increase of kinetic energy and mobility of the atoms due to collision and production of minimum number of lower energy electrons resulted to increase the plasma density which in turn multiplies flux of the atoms arriving at the substrate surface per unit time and hence increase the growth rate and thickness of film to 960 nm. Increasing RF power to 200 W yielded highly energetic secondary electrons for more $Ar^+$ ions bombardment. Secondary electron emission affected the rate of growth of the sputtered film and these secondary electron accelerated the plasma towards the substrate causing macro effect i.e., reduction on the film thickness [31]. Hence thickness of the film got reduced to 480 nm. In addition it affects the film property which is schematically shown in Fig. 1.

### 3.2. Structural properties

The XRD pattern of CdO thin films deposited on glass substrates as a function of sputtering RF power is shown in Fig. 2. From this figure, the sharp diffraction pattern reveals that the deposited films are polycrystalline in nature exhibiting predominant orientation along (111) plane at position $2\theta = 32.9^\circ$ with RF power up to 150 W. The XRD patterns are in good agreement with Joint committee powder diffraction system (JCPDS) File No: 050640 which indicate that the CdO thin films are cubic structure ($Fm\bar{3}m$ space group) and the atoms are arranged in face centered lattice (FCC) arrangement. The intensity of the (111) plane gets increased with an increase of sputtering power to