Optical and Electrical properties of Sn-Doped Cadmium Oxide Thin Films Grown by Chemical Bath Deposition Technique
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Abstract
The structural, optical and electrical properties of the films at different doping concentrations of 0, 2, 4, and 6 % have been investigated using chemical bath deposition technique. Cadmium acetate di-hydrate was used as precursor for preparation of the CdO thin films and Tin (II) chloride was employed as a tin source. The XRD patterns revealed a polycrystalline having the characteristic peaks of cubic structure. Transmittance of the CdO films increases with increasing Sn dopant in the films, and the maximum transmittance of 84% was seen at 4% doping concentration. The above observation was confirmed by AFM study which depicts uniform and homogeneous, thin films at 2 and 4 % at Sn doping concentrations. The average bandgap energy of tin oxide was 2.30 eV and this value is bigger than that of pure CdO 2.22eV. This implies that the tin doping can be used as a regulator of the bandgap of CdO films. Hall mobility, carrier density of Sn: CdO films show variation with Sn: CdO doping concentration such that carrier concentration and mobility show the maximum at 4% doping concentration. The films grown at 4% in this work is a promising candidate for solar cell applications.

Keywords: Cadmium oxide, tin, electrical, transmittance, optical band gap.

1. Introduction
There is an ever growing interest in the synthesis of low-cost, non-vacuum transparent conducting oxides (TCOs) with n-type conductivity [1]. 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 [2]. Transparent conducting oxide thin films of CdO has been deposited on to glass substrates using chemical bath deposition (CBD) [3]. Among these TCO, cadmium oxide (CdO) has received considerable attention for solar cell application due to its low electrical resistivity and high transparency in the visible range of solar spectrum [4-5]. Different techniques such as sol-gel [6], DC magnetron sputtering [7], radio frequency sputtering [8], spray pyrolysis [9] chemical vapor deposition [6], chemical bath deposition [2-3], and pulsed laser deposition [10-11] have been used to deposit CdO thin film. CdO micro particles undergo bandgap excitation when exposed to UV-A light and is also selective in phenol photo degradation [12]. It has a high electrical conductivity that is attributed to moderate electron mobility and higher carrier concentration due to the contribution from shallow donors resulting from inherent non-stoichiometry. Non-stoichiometric undoped CdO thin films usually exhibit low resistivity [13, 16] and n-type degenerate semiconductor with high electrical conductivity (10^2 to 10^4 S/cm) due to native defects of oxygen vacancies and cadmium interstitials [6, 14-16].

Generally, the optical and electrical property of the thin films are dependent on its oxidation state, the amount of dopant materials, and the fabrication process [14]. It was reported that when CdO is doped with rare earth oxides, its optical bandgap can be widened [17]. This can be largely achieved by doping it with foreign impurities [15]. León-Gutiérrez et al. [18] prepared CdO thin films using chemical bath deposition method. Furthermore, Fluorine-doped CdO thin films were prepared by sol-gel process with various atomic ratios of Cd: F to improve its electrical and optical properties [19], it was reported that the 10% fluorine-doped film prepared with pH 8 precursor solution showed the lowest resistivity of 0.01574 Ω cm [19]. In another research work, the effects of Te-doping on the structural, morphological and optical properties of the CdO thin films were studied by [20]. Optical results indicate that 1 % Te-doped CdO thin film has the maximum transmittance of about 87 %, and the values of optical energy band gap increases from 2.50 to 2.64 eV with the increase of Te-doping ratio [21]. Furthermore, [22] prepared cadmium oxide thin films of zinc with different concentrations of Zn-doping levels i.e. (0, 2, 4, 6, and 8 at%). The band gap value increases with Zn doping and reaches a maximum of 2.65 eV for the film coated with 8 at% Zn doping and for further higher doping concentration it decreases [22].

Sn (Sn) is another dopant that if doped with cadmium oxide could improve both its optical and electrical properties of the materials [1]. One of the most favored dopants is tin which substitutes the cadmium cations. Sn was chosen in this work as dopant to control and enhance the properties of CdO thin films. Sn⁴⁺ ion has four valence electrons (5s², 5p⁰) and the ionic radius of Sn⁴⁺ (0.69 Å) is slightly smaller than that of Cd²⁺ ions (0.95 Å), thus we expect that Sn⁴⁺ ions doping in CdO will lead to improvement in electrical conductivity by increasing electron concentration [4]. Also, Sn³⁻ has an ionic radius of 83pm while Cd⁶⁺ has 109 pm. Since Sn³⁻ has lower ionic radius than that of Cd, there would be considerable enhancement in its electrical property [24]. This is achievable by a shift in the optical band gap along with the increase in transparency of CdO films [23]. CdO thin films have been doped with tin to improve optical and electrical properties in the literature. [5, 23] fabricated tin-doped cadmium oxide (CdO: Sn) using atmospheric pressure metalorganic chemical vapour deposition technique: the result showed highly transparent and conductive CdO: Sn thin films are promising for photovoltaic applications [5]. The effect of doping on the physical properties of CdO thin films was reported by a Zheng et al. [24].

There are a number of techniques that can also be employed to grow cadmium oxide (CdO) including Chemical Vapor Deposition [6], SILAR [25], Thermal evaporation [16], Sol-Gel Process, [19-20][26][34], SPEED [27], DC Reactive Magnetron Sputtering [28-29], Spray Pyrolysis [8-9, 22, 30-33, 37], Pulsed Laser Deposition [9, 27, 36], The control over the properties of cadmium oxide through chemical route has attracted increasing interest and can be easily achievable through chemical bath deposition technique. CBD [12, 16] is the most successful and best method to obtain low cost CdO thin films that have optimal features for photovoltaic device applications because of it is an efficient, cost effective, and
availability. This technique was however used to deposit high quality CdO films by controlling its optical and electrical properties for solar cells applications.

2 Experimental Details

Cadmium Oxide (CdO) thin films were deposited onto clean glass substrates using the Chemical Bath Deposition (CBD) technique. Cadmium acetate di-hydrate (Merck 99.9%) was used as precursor for preparation of the CdO thin films as Cd$^{2+}$ ion source and Tin (II) chloride was employed as a tin source. All chemicals used were of Analytical Grade. Before deposition of the films, glass substrates were cleaned thoroughly with industrial soap, rinsed with deionized water followed by acetone, then rinsed again with deionized water and dried [19]. This process was carried out to ensure clean surface essentially for the formation of nucleation centres that is required for thin film deposition. 0.2 M of cadmium acetate di-hydrate were dissolved in 0.25 M of methanol with a constant magnetic stirring. 35 ml of deionized water was added to the solution until the clear homogeneous solution was obtained. For Sn doping, Tin (II) chloride di-hydrate was then dissolved in the solution at different percent (0, 2, 4 and 6 %). The final solution was then stirred for 1 h and kept at 85°C temperature. A clear and homogeneous solution was seen. The cleaned substrates were then inserted and held vertically in the reaction bath for 24 hours for the deposition to complete [29].

The Film thickness was determined by gravimetric weight difference method using high precision electronic balance.

UV-VIS Spectrophotometer (Perkin Elmer) was used to characterize the optical properties of the films. The electrical characterization of the samples was carried out by the Hall Effect measurement using the Vander-Paw configuration at room temperature. Crystalline phases of CdO films were characterized by X-ray diffraction using a Rigaku X-ray diffraction (XRD) system (with 40kV, 30 mA CuKα radiation, λ = 0.154406 nm). The XRD pattern of the films for 2θ values are recorded at a range from 15 to 85°. The XRD peaks were compared with JCPDS cards for phase identification. The AFM images of the CdO films deposited at different doping conventions were measured with AA 3000, Angstrom Advanced Inc.

3 Results and Discussions

Fig 1 shows the X-ray diffraction pattern of CdO films deposited at different Sn doping concentrations. All CdO thin films were transparent, have good adhesion to substrate, better uniformity, free from pinhole and were stable for long period when kept in atmosphere. The XRD revealed diffraction peaks at (111), (200), and (220) which corresponds to polycrystalline having the characteristic peaks of cubic structure of CdO (JCPDS Card No. 73-2245). Other disenable planes are (311) and (222) but with lower intensities. The CdO films have (111) plane as preferred orientation. Similar observation was also reported by [2].

![XRD at different Sn doping concentrations](image)

(a) 0% of Sn (b) 2% of Sn (c) 4% of Sn (d) 6% of Sn

Fig. 2 shows the transmission curve of CdO films deposited as a function of Sn doping concentrations. At 300-550 nm. Average transmittance in the visible region generally increases as Sn doping level increases. At 0%, 2%, 4%, 6% doping levels, average transmittance are: 75 %, 83%, 84%, and 74 % respectively. Lowest value of transmittance observed at 6% doping level may be due to excess Sn atom in the Sn: CdO interstitial sites. On the other hand, low value of transmittance observed at 0% may be attributed to disproportionate of Sn atom to balance Cd atom in the Sn: CdO interstitial sites. The films deposited at 2% and 4% have transmittance above 80% and is due to correct proportion of Sn atom to replace Cd atoms in their intestinal sites. They can therefore be useful for window layer of a solar cell.

![Transmission curve of CdO thin films at different Sn concentrations](image)

(a)

http://www.jfips.com/
Sn doped CdO film. The average optical bandgap energy of pure CdO film was calculated to be 2.30 eV. The optical band gap for 0%, 2%, 4%, 6% are: 2.27, 2.29, and 2.33 eV. The optical bandgap energy of tin-doped CdO films increased with the increase in the tin-doping with maximum at 4 at%. Further increase in concentration to 6% leads to decrease in optical bandgap. It is consequence of the structural improvement and the size quantization which leads to change in optical properties of the metal oxide nanostructures [15]. Moreover, the average bandgap energy of tin oxide obtained in this work which about (2.30 eV) is bigger than that of pure CdO 2.22 used in the present work. The bandgap of tin-doped CdO which is bigger than the bandgap of pure CdO means that the tin doping can be used as a regulator of the bandgap of CdO films. Similar types of behavior of change in band gap after Sn, Ga and Cu doping were reported in the literature [6]. They have described increase in bandgap after doping. Higher band gaps are required for any optoelectronic application, particularly for solar cell applications. The blue-shift of energy band gap appeared due to electrons populated states within the conduction band which pushes the Fermi level to higher energy and related to the Burstein–Moss effect [24, 25]. Change in the band structure of the films and creation of new donor levels in the forbidden band gap can also be observed that the band gap starts to increase as Sn doping increases. This may also be due to Burstein–Moss effect. This effect occurs when the carrier concentration exceeds conduction band edge density of states, which corresponds to degenerate doping in semiconductors. As the doping concentration increases, more and more donor states are produced which pushes Fermi level higher in energy [24, 26]. The Moss–Burstein shift in the band-gap value is given by equation (1).

\[
\Delta E = \frac{k^2}{2m^*} \left(3\pi^2n\right)^{2/3}
\]

(1)

Where \(k\) is the reduced Planck constant, \(m^*\) is the effective electron mass with respect to the free electron mass and \(n\) is the free electron concentration in a single valley.

Fig. 4: Plots of \((\alpha h\nu)^2\) versus photon energy \(h\nu\) for CdO: Sn thin films

Fig. 5 shows the variation of hall mobility, carrier density and resistivity of Sn: CdO films. It can be seen that the electrical parameters were strongly influenced by Sn doping in the CdO films. As the Sn concentration increases from 0 to 6%, the resistivity decreases from \(5.56 \times 10^{-2}\) \(\Omega\text{-cm}\) to the minimum value of \(3.01 \times 10^{-4}\) \(\Omega\text{-cm}\) this value is slightly lower than the obtained resistivity using pulsed laser method [21] and that of a report which obtained \((3.1 \times 10^{-4}\) \(\Omega\text{-cm}\) with metal organic chemical vapor deposition [27]. Similarly, there is relative improvement on the carrier concentration results. The improvement may originate from the replacement of Cd\(^{2+}\) ions by Sn\(^{4+}\) ions in the CdO lattice. The maximum mobility \(4m^2/Vs\) was obtained at 4% Sn concentration as well as lowest resistivity. As is well known, resistivity is proportional to the reciprocal of the product of carrier concentration and mobility. The reduction of electrical resistivity may due to reduction of voids and improved carrier concentration. The electrical conductivity and mobility is more sensitive for grain interface than defects of crystals. It is
observed that carrier concentration and mobility initially increase with maximum at 4% Sn: CdO doping concentration. Resistivity decreases with minimum value of 3.1 x 10^-4 Ωcm at 4% Sn: CdO doping concentration which corresponds to 22 x10^5 cm² and mobility of 15x cm² V^-1 s^-1 respectively [28, 35, 36]. These values indicate the maximum value for optimum concentration for possible applications. Hall measurements indicate the CdO films to be of n-type semiconductors. The initial decrease in resistivity is attributed to an increase in free carrier concentration due to the substitutional incorporation of Sn ions at O^2- anion sites. However, for films with higher doping concentration, the free carrier concentration saturates and the mobility slightly decreases due to the formation of Cd-Sn complexes in the grain boundaries, leading to a slight increase in the resistivity of the CdO films [29, 37].

4 Conclusion

This work investigates the optical and electrical properties of CdO thin films doped with different concentrations of CdO: Sn (0, 2, 4, and 6 %) using chemical bath deposition technique. The XRD patterns revealed a polycrystalline having the characteristic peaks of cubic structure of CdO. Transmittance of the CdO films increases with increasing Sn dopant in the films, and the average transmittance in the visible region (300-550 nm) has been found (75 %, 83%, 85%, 74 %) for the tin doping (0, 2, 4, 6 %) respectively. These observations were confirmed with AFM studies which exhibits granular morphologies which roughness which varied with doping content. The grain size of the films ranges from 0.21μm to 0.46 μm based on Sn: CdO doping concentrations. Hall mobility, carrier density of Sn: CdO films show variation with Sn: CdO doping concentration such that carrier concentration and mobility increase until maximum at 4% Sn: CdO, additional increase in concentration led to decrease in carrier concentration and mobility. Resistivity decreases with minimum at 4% Sn: CdO doping and increases with further increase in doping concentration.

References