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Optical and Electrical Properties of CdO: Sn Thin Films for Solar Cell Applications

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Abstract Tin doped Cadmium Oxide (CdO:Sn) thin films were successfully deposited by thermal evaporation in the Edward's Auto 306 Magnetron Sputtering System. Their optical and electrical properties were studied using Solid Spec-3700 DUV Spectrophotometer and Four Point Probe respectively. The optical properties of CdO:Sn thin films showed high transparency in the visible region of the electromagnetic spectrum which varied with Sn doping, this makes CdO:Sn an excellent candidate for optoelectronic applications such as a window layer. Undoped Cadmium Oxide (CdO) thin films were also prepared for comparison with tin doped Cadmium Oxide thin films. Doped and undoped Cadmium Oxide had a transmittance of 70-85% and 50-89% respectively. Band gap energy for undoped CdO was 2.43eV while that of tin doped CdO ranged between 3.19-3.29eV for tin doping of 1-7%. Resistivity of undoped and Tin doped Cadmium Oxide ranged between 16-93Ωcm.

Keywords Thermal evaporation, Tin doping, Optical properties, Electrical properties

1. Introduction

Energy consumption has increased steadily with civilization. Energy crisis due to a decline in fossil fuel stocks and increasing carbon dioxide emissions that are causing global warming has enhanced interest in the development of clean renewable sources of energy. To sustain human development, more electrical energy consumption is expected in future [1]. Solar cells hold great hopes for use as an environmental friendly and economically viable renewable source of energy.

Cadmium Oxide (CdO) is an important semiconductor material for the development of various technologies of solid-state devices. The semiconducting thin films of CdO are transparent in visible and NIR spectral regions [2]. Cadmium Oxide is an n-type semiconductor with Sodium Chloride structure. It has a direct optical band gap of 2.3 eV. 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 due to native defects of Oxygen vacancies and Cadmium interstitials [3]. Optically, it is a transparent material over energies of 540 nm in the solar spectrum. Cadmium Oxide thin films find wide applications in the field of optoelectronic devices such as solar cells, transparent electrodes, photodiodes among others. For example CdO transparent conducting oxide prepared by [4] with a band gap of 2.3 eV and an electron affinity of 4.5eV were used for fabricating CdO/CdTe heterostructure solar cells with efficiencies of 9.1% by DC magnetron sputtering.

The conduction of pure CdO is attributed to its native defects of Oxygen vacancies and Cadmium interstitials. Therefore, the conductivity of CdO thin films can be controlled by those native defects through the procedure of thin film preparation including doping with metallic ions. Cadmium Oxide can be doped with various dopants for example fluorine and tin. Fluorine doping of CdO, shifts the optical band gap along with the increase in transparency of CdO films. Tin-doped Cadmium Oxide (CdO:Sn) deposited by [5] using atmospheric pressure metalorganic chemical vapour deposition technique, showed that the highly transparent and conductive CdO:Sn thin films are promising for photovoltaic applications. The structural, electrical and optical properties of the fabricated thin films were influenced by partial pressure of Dimethylcadmium and Tetramethyltin, substrate temperature, film thickness and annealing conditions. A sheet resistance of (14-17) Ω/square units were obtained for as-deposited CdO:Sn thin films with a thickness of (120-150) nm. The transmission of the films in the visible range was high (80-95) % and shifted towards the blue region due to the Moss-Burstein (M-B) effect. The films exhibited direct and indirect band-to-band transitions, which corresponded to optical band gaps of 3.0 and 2.5eV, respectively. The electro-optical properties of as-deposited CdO:Sn thin films were further improved by post-deposition

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annealing. A resistivity value of (1.4-1.6) x 10^{-4}Ωcm was obtained after annealing in Helium and Hydrogen ambient.

CZT/CdO cells were categorised in two groups [6], namely type A and B. A: SnO_2/CdO/CZT structure, B: SnO_2/CdS/CdO/CZT structure. In type A, evaporation of CdO led to the formation of CdO/SnO_2 junctions which had V_{oc} in the range of 100-250 mV. The current densities of devices made were in the range of 4-6 mA/cm^2. Type B devices had higher current densities ~8mA/cm^2. The V_{oc} were in the range of (200-280) mV. This showed that carrier concentration varied with the proportion of Cadmium in the cell.

Tin doped CdO thin films prepared by [7] using electron beam technique exhibited direct band-to-band transitions, which corresponded to optical band gaps of 3.1– 3.3 eV with a transmittance value of ~83% and a resistivity value of 4.4×10^{-4} Ωcm were achieved for $(CdO)_{0.88}(SnO_2)_{0.12}$ film annealed at 350^{0}C for 15 minutes, whereas the maximum value of transmittance ~93% and a resistivity value of 2.4×10^{-3} Ωcm were obtained at 350^{0}C for 30 minutes.

Transparent conducting CdO:Sn films deposited by [8] Metal Organic Chemical Vapour Deposition for application in CdTe/CdS solar cells had a conversion efficiency of 14.3%. The films had a sheet resistance of 14-17Ω/square for a film of thickness of 120-125 nm.

The effect of substrate temperature studied by [9] on electrical and optical properties of CdO:Sn deposited by Pulsed Laser Deposition Technique found that the films were highly transparent (78-89%) in the visible region. The resistivity increased with growth temperature and the lowest resistivity of 1.96 x 10^{-5} Ωcm was observed for the films grown at 150^{0}C. These highly conducting and transparent tin-doped CdO thin films could be an excellent candidate for current and future solar cell applications.

2. Experimental Procedure

Reactive thermal evaporation of CdO and CdO:Sn thin films was done in Edwards Auto 306 Magnetron Sputtering System. To prepare Cadmium Oxide, Cadmium was heated in glass tube until it melted. It was allowed to cool in sealed glass tube to prevent oxidation of Cadmium. Clean glass substrates were then mounted on a substrate holder of the Edwards Auto 306 Magnetron Sputtering System. About 1g of Cadmium was placed on a boat and then the chamber covered tightly and evacuated. A constant current of 3.0A was supplied to the heater to evaporate the material in presence of oxygen at a flow rate of 20 sccm and a chamber pressure of 3.8 x 10^{-5} mbar form CdO thin films.

To prepare CdO:Sn thin films, Cadmium and Tin were mixed at predetermined ratios (Tin doping ranging from (1-7)%. Cadmium and Tin were heated in glass tubes until they melted. They were allowed to cool in sealed glass tubes to prevent oxidation of Cadmium and Tin. Clean glass substrates were then mounted on a substrate holder of the Edwards Auto 306 Magnetron Sputtering System. About 1g of Cadmium and Tin alloy were placed on a boat and then the chamber covered tightly and evacuated. The deposition conditions for the films are shown in table 1.

Table 1. Deposition parameters of CdO:Sn thin films

Parameter	Units
Oxygen flow rate	20 sccm
Sn doping	1, 2, 3, 4, 5, 6, 7%
Deposition temperature	453 K
Base pressure	3.8 x 10^{-5} mbars
Heater current	3.0 A
Heater to boat distance	15.0 cm

3. Results and Discussions

3.1. Transmittance of CdO and CdO:Sn

Transmittance of undoped CdO was between 70-90 % for photons of wavelength between 350-800 nm while that of 1-7 % Sn doped CdO was between 62-89 % for photons of wavelength between 350-800 nm. Transmission values between 83-89% were obtained for photons of wavelength 500-628nm for 1- 4% Sn doped CdO samples. However, when Sn concentration increased beyond 5% the transmission spectra decreased, this is probably due to the disorder in the lattice which increases in the localized states near the bands. High transmittance values of Sn doped CdO thin film samples is a clear indication that CdO:Sn is appropriate for use as a window layer in photovoltaic applications. The transmittance spectra of doped and undoped CdO are shown in figure 1.

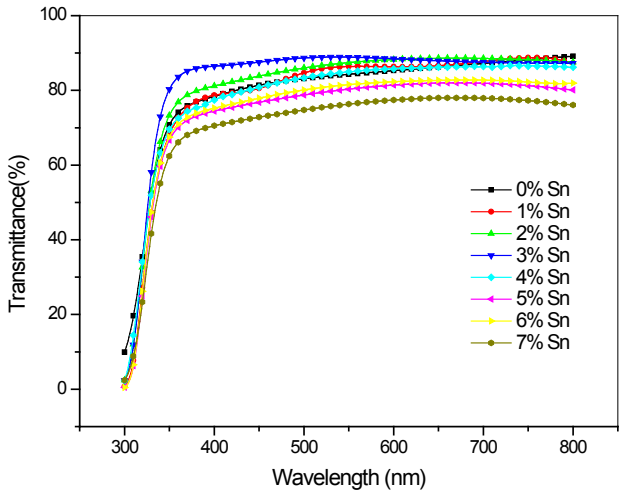

Figure 1. Transmittance spectra of 0-7% Sn doped CdO

It is observed that the transmission improved significantly after tin doping due to the shift in the absorption edge. Variations in percentage of optical transmittance in different studies show that optical transmittance is strongly dependent on the kind of metal dopant, the method of thin film deposition and deposition conditions.

3.2. Energy Band Gap of CdO and CdO:Sn

The band gap, E_g was extracted from transmittance data simulated using SCOUT 2.4 software. Energy band gap can also be obtained from straight line plots of $(Ah\upsilon)^{2/n}$ as a function of $h\upsilon$: an extrapolation of the value of $(Ah\upsilon)^{2/n}$ to zero, also gives E_g. If a straight line for n=1 is obtained, then there is a direct electron transition between the states of the semiconductor, whereas for n=4, the electron transition is indirect. The variation of optical band gap with tin doping is shown in figure 2.

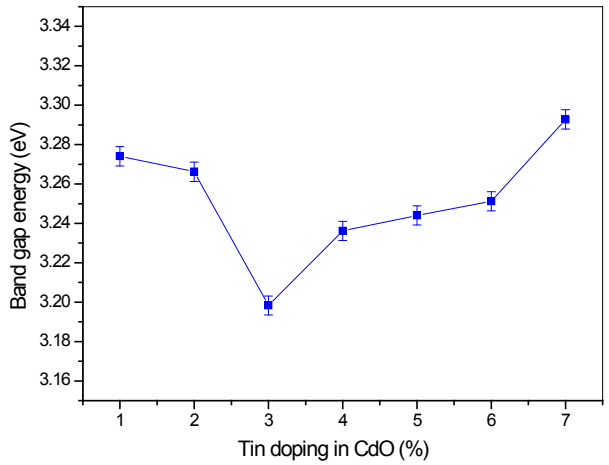

Figure 2. Variation of band gap energy of CdO thin films with tin doping

Energy band gap of doped CdO ranged between 3.19-3.29 eV. Energy band gap values reported by [3] are between 3.0-3.20 eV and those reported by [10] ranged between 2.90-3.30 eV. Decrease in band gap from 1-3 % Sn doping may be attributed to the shift in the Fermi-level hence change in the band structure of the films and creation of new donor levels in the forbidden band gap.

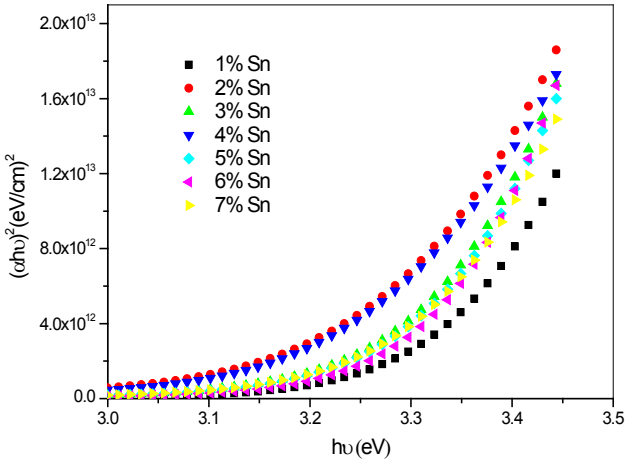

Figure 3. Plots of $(\alpha h\upsilon)^2$ versus photon energy $h\upsilon$ for CdO:Sn thin films

The increase in band gap from 3-7 % Sn doping may be attributed to the 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 [11]. The Moss–Burstein shift in the band-gap value is given by equation (1).

$$\Delta E = \frac{\hbar^2}{2m^*}(3\pi^2 n)^{\frac{2}{3}} \quad (1)$$

Where ħ, 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.

The variation of absorption spectra with photon energy is shown in figure 3.

Undoped CdO thin films were also prepared for comparison with doped CdO. The films had an energy gap of 2.43 eV. The optical energy band gap obtained is within range of that reported by [2] and [12] which ranged between 2.2-2.7 eV and 2.32-2.54 eV respectively. It is therefore noted that tin doping of CdO increased the band gap energy of undoped CdO. The variation of absorption spectra for undoped CdO with optical energy band gap is shown in figure 4.

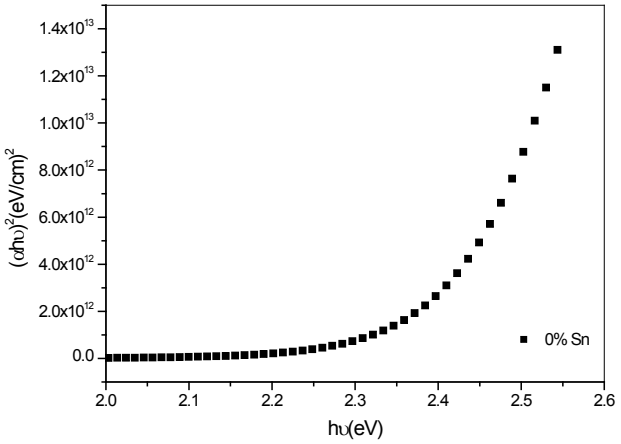

Figure 4. Plot of $(\alpha h\upsilon)^2$ versus photon energy $h\upsilon$ for undoped CdO thin films

4. Electrical Resistivity of CdO and CdO:Sn

Sheet resistance was measured using Four Point Probe. Resistivity of CdO and CdO:Sn ranged between (16 - 93) Ωcm. The variation of resistivity with tin doping is shown in table 2 and figure 5.

Reduced resistivity from (0-2)% Sn doping of CdO is attributed to replacement of cadmium atoms by tin atoms in the CdO crystal yielding two free electrons from each atom and occupation of interstitial positions there by contributing up to four free electrons. The replacement of Cd^{2+} ions by Sn^{+4} ions in CdO lattice liberates two free electrons in conduction band which enhances the carrier concentration significantly [13].

Similar trend in resistivity was observed by [13] for CdO:Sn thin films prepared by Pulse Laser deposition,

resistivity decreased as Sn concentration increased to 2.9% and then increased as Sn concentration increased further to 7.6%.

Table 2. Electrical properties of CdO thin films with tin doping

% of Sn in CdO	Sheet resistance $x10^5 \pm$ 500 Ω/υ	Resistivity x 10^1 (Ωcm)
0	6.48	4.2
1	4.16	2.7
2	2.47	1.6
3	2.78	1.8
4	4.94	3.2
5	8.17	5.3
6	11.41	7.4
7	14.34	9.3

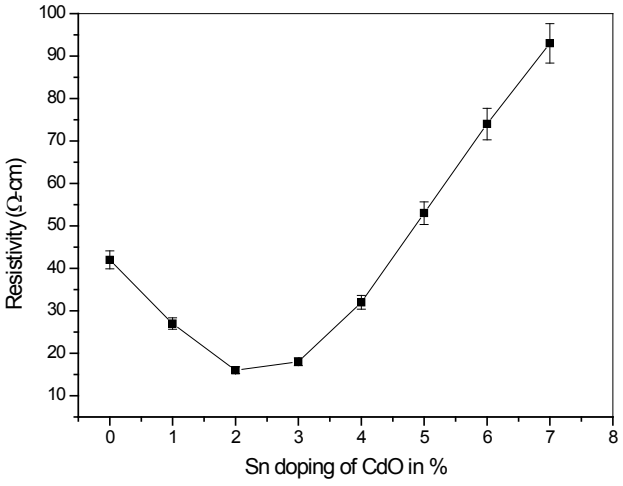

Figure 5. Variation of electrical resistivity of CdO:Sn thin films with tin doping

As Sn doping increased beyond 3% the resistivity of doped CdO increased. This could be attributed to coexistence phases of Sn doped CdO, cubic CdO being the predominant one and an amorphous admixture of Cadmium Oxide and Tin Oxide [12].

It is evident from figure 5 that electrical resistivity of CdO strongly depend on the tin doping and deposition method and conditions like substrate temperature, deposition pressure, amount of doping among others as the resistivity obtained in this study varies from reported resistivity values in other studies.

5. Conclusions

Undoped CdO and Tin doped CdO thin films were successfully deposited on glass substrate using thermal evaporation and reactive thermal evaporation respectively under different deposition conditions. The effects of 0-7% Sn doping of CdO on optical and electrical properties of CdO respectively were investigated.

The transmittance increased and the resistance dropped as the Sn doping is increased from 1-3% due to creation of impurity states in the forbidden energy gap. Further increase of the doping level results in the phase segregation and a band filling which impact the sheet resistance and transmittance respectively.

Since Sn doping improved optical and electrical properties of CdO, Sn doped CdO thin films have potential applications as Transparent Conducting Oxide material in photovoltaic cells and other optoelectronic device applications.

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