

PREPARATION, ELECTRICAL PROPERTIES AND OPTICAL CHARACTERIZATION OF Cd_2SnO_4 AND CdIn_2O_4 THIN FILMS AS TRANSPARENT AND CONDUCTIVE COATINGS*

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(Received March 23, 1987)

Transparent and conductive Cd_2SnO_4 and CdIn_2O_4 thin films have been prepared by reactive sputtering from Cd–Sn and Cd–In alloy targets in an $\text{Ar} + \text{O}_2$ atmosphere. Electrical conductivities of the order of $10^5 \Omega^{-1} \text{m}^{-1}$ with the optical transmission as high as 90% were easily attained. Hall and thermoelectric power measurements indicate that charged point defects are responsible for the scattering of conduction electrons. The optical constants of the films were computed from the transmission and reflection measurements in the visible and near-IR spectral ranges using a special procedure based on a model of an inhomogeneous film with a rough surface.

1. INTRODUCTION

Thin films of the ternary oxides Cd_2SnO_4 and CdIn_2O_4 show extremely promising properties such as low, metal-like electrical resistivity, good transmissivity in the visible range of the light spectrum and high reflectivity in the near-IR^{1–9}. In comparison with thin metallic films, *e.g.* copper, gold and silver, they are much more stable and wear resistant. They can be used, similarly to the well-known $\text{In}_2\text{O}_3:\text{Sn}$ films, as transparent electrodes and heat mirrors in optoelectronics and solar energy conversion technology.

In this work we want to show that Cd_2SnO_4 and CdIn_2O_4 films can be easily obtained by reactive sputtering in a form of highly degenerate, transparent semiconductors. Hall effect and thermoelectric power (TEP) as well as spectrophotometric measurements in the visible and near-IR regions are discussed in order to characterize the optical properties of these films and to establish the transport mechanism of charge carriers.

* Paper presented at the 14th International Conference on Metallurgical Coatings, San Diego, CA, U.S.A., March 23–27, 1987.

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2. FILM PREPARATION AND CHARACTERIZATION

Cd_2SnO_4 and CdIn_2O_4 films were prepared by ion sputtering from metallic alloy targets in a reactive $\text{Ar} + \text{O}_2$ atmosphere. Most of the films were obtained by d.c. sputtering, although some of CdIn_2O_4 samples were deposited using an r.f. power system¹⁰. The d.c. sputtering conditions were as shown in Table I^{7,10,11}. The composition of the reactive $\text{Ar} + \text{O}_2$ gas mixture could be controlled in a wide range (0%–100% O_2), as oxygen and argon were introduced into the sputtering chamber independently through two needle valves. For oxygen concentrations greater than 5% the films were transparent and conductive.

TABLE I
D.C. SPUTTERING CONDITIONS

	Cd_2SnO_4	CdIn_2O_4
Target	60 at.% Cd + 40 at.% Sn	66 at.% In + 34 at.% Cd
Discharge voltage	1.6 and 2.0 kV	2.0 kV
Discharge current density	6–15 A m^{-2}	10.5–16.6 A m^{-2}
Target-to-substrate spacing	35 mm	35 mm
Total pressure	6 Pa	6 Pa

Some of the samples were also subjected to a post-deposition heat treatment in vacuum, air and hydrogen. The process of heat treatment does not lead to any remarkable changes in the structure and composition of the films. However, it is still possible to change the concentration of point defects by an appropriate annealing procedure and therefore to modify the electrical properties of the films (see below).

X-ray diffraction analysis revealed that the films were mostly polycrystalline with the majority of cubic spinel phase. The lattice constants were as follows^{10–12}:

$$\text{Cd}_2\text{SnO}_4 \quad a = 0.9172\text{--}0.9206 \pm 0.0009 \text{ nm}$$

$$\text{CdIn}_2\text{O}_4 \quad a = 0.9166\text{--}0.9202 \pm 0.0005 \text{ nm}$$

For a discharge power density lower than 2 W cm^{-2} cadmium stannate films were amorphous (Fig. 1, curve b).

As it can be seen in Fig. 1, the X-ray pattern contains not only Cd_2SnO_4 lines but also shows evidence of the formation of CdSnO_3 and SnO phases. For higher oxygen concentrations in the reactive gas mixture additional lines, for CdO , were observed⁵.

In the case of cadmium indate films the diffraction patterns consisted mainly of CdIn_2O_4 lines and only a small concentration of In_2O_3 phase was detected.

3. HALL EFFECT

Hall effect measurements were carried out in the temperature range from 80 to 400 K for both "as-sputtered" and heat-treated films. The temperature dependences of the carrier concentration and of Hall mobility for Cd_2SnO_4 films are shown in Figs. 2 and 3. Most of the films behave like typical degenerate semiconductors, i.e. their carrier concentration does not change with temperature. The dependence of

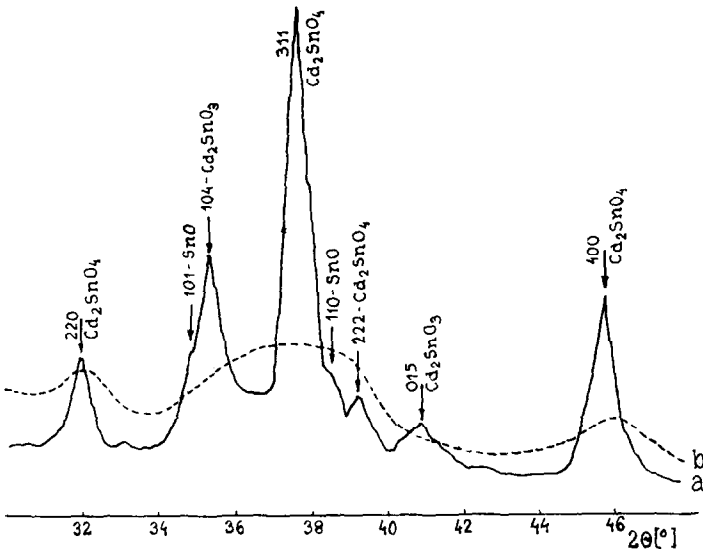


Fig. 1. X-ray diffraction patterns for Cd_2SnO_4 films: curve a, 3 W cm^{-2} discharge power density and 70% O_2 in the reactive $\text{Ar} + \text{O}_2$ gas mixture; curve b, 1.2 W cm^{-2} discharge power density and 50% O_2 in the reactive $\text{Ar} + \text{O}_2$ gas mixture.

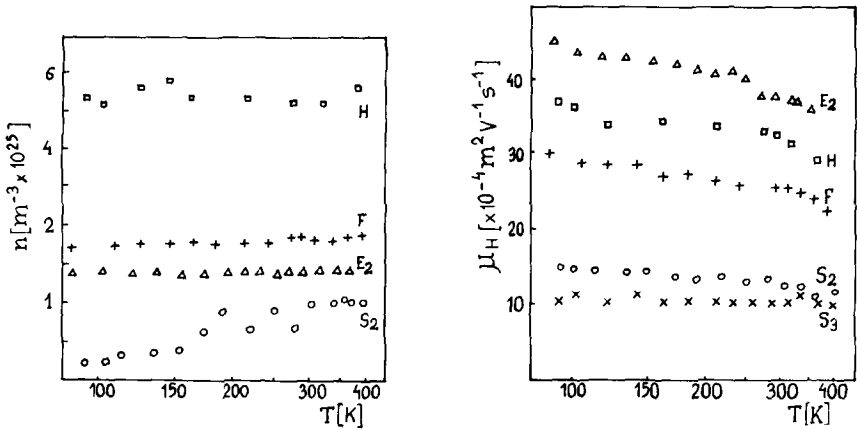


Fig. 2. Carrier concentration vs. temperature for thin Cd_2SnO_4 films. Sputtering conditions for the films: H, F, E_2 and S_2 : discharge power density 1.2 W cm^{-2} , 3 W cm^{-2} , 1.7 W cm^{-2} , 1.7 W cm^{-2} and oxygen content in the reactive $\text{Ar} + \text{O}_2$ gas mixture 50%, 80%, 70%, 70%, respectively.

Fig. 3. Hall mobility vs. temperature for thin Cd_2SnO_4 films.

the Hall mobility on temperature is also very weak. At higher temperatures and for the samples with the highest mobilities, the Hall mobility has a tendency to drop with temperature, thus indicating the influence of scattering by acoustic phonons.

In general, the results of Hall measurements for CdIn_2O_4 films¹³ are similar to those for Cd_2SnO_4 . Cadmium indate films obtained by r.f. sputtering are less conducting than the films deposited by d.c. sputtering and they exhibit a noticeable dependence of the carrier concentration on temperature (the activation energy of

donor levels is about 0.01–0.04 eV). The dependence of Hall mobility on temperature for r.f.-sputtered CdIn_2O_4 films is clearly pronounced and in the limit of low carrier concentrations one can obtain $\mu_H \propto T^{3/2}$. This kind of temperature dependence is typical of electron scattering by ionized impurities¹⁴.

Detailed investigations of the influence of post-deposition heat-treatment on the electrical properties of the films showed that in the case of Cd_2SnO_4 , annealing in vacuum at 10^{-4} Pa and 670 K caused an increase in both Hall mobility and carrier concentration. Subsequent reduction process in hydrogen at 670 K resulted in a further increase in electron concentration and a slight decrease in mobility.

In order to explain this behaviour one must take into account the fact that the films deposited by sputtering are generally non-stoichiometric. The non-stoichiometry results from the formation of point defects that include oxygen vacancies and metal interstitials as well as oxygen traps at grain boundaries. Annealing in vacuum causes both the generation of oxygen vacancies and the ordering process in the film (ordering understood as an increase in the degree of preferred crystallographic orientation and desorption of oxygen from grain boundaries). Oxygen vacancies play the role of donors, thus affecting the concentration of conduction electrons. The ordering process also leads to an increase in the mobility of charge carriers.

The subsequent reduction in hydrogen causes a further increase in electron concentration. The decrease in electron mobility in this case probably results from the increase in the effective mass of the charge carriers.

As only small concentrations of secondary phases (e.g. In_2O_3 in cadmium indate films) were detected, these phases should not be considered as fundamental in the process of electron scattering, especially for films deposited by d.c. sputtering.

4. THERMOELECTRIC POWER MEASUREMENTS

The TEP (Seebeck coefficient) was measured in the temperature range from 300 to 400 K in the configuration shown schematically in Fig. 4.

Two copper–constantan thermocouples attached to the ends of a sample served for the measurement of both the temperature difference ΔT (switch S in

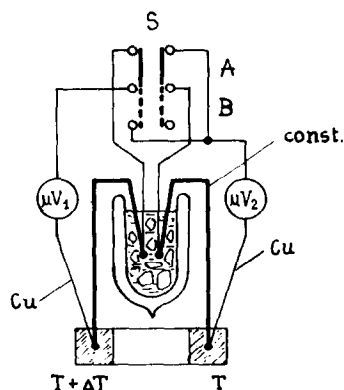


Fig. 4. Schematic diagram of the experimental set-up for TEP measurements.

position A) and the thermal e.m.f. in the film–copper circuit (switch S in position B). The reference junctions of the thermocouples were electrically insulated and placed in an ice–water bath at 273 K. A temperature difference ΔT of a few kelvins between cold and hot ends of the sample was maintained by means of a special gradient heater. Typical plots of the TEP for Cd₂SnO₄ and CdIn₂O₄ films are shown in Fig. 5.

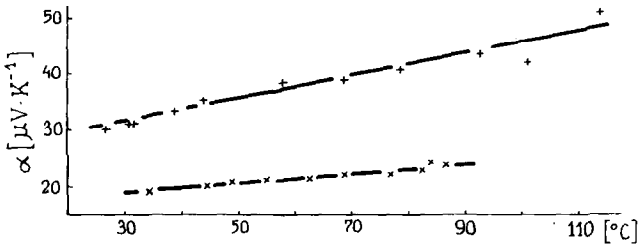


Fig. 5. Thermoelectric power vs. temperature for a CdIn₂O₄ film with an electron concentration $n = 1.2 \times 10^{26} \text{ m}^{-3}$ (+) and for a Cd₂SnO₄ film with $n = 2.3 \times 10^{26} \text{ m}^{-3}$ (x).

The measurements indicate that the TEP α_e is proportional to the temperature, as one would expect for a degenerate semiconductor¹⁴:

$$\alpha_e = \frac{\pi^2 k^2 T}{|e| E_F} \left(\frac{1}{2} + \frac{1}{3} p \right) \tag{1}$$

where E_F is the Fermi energy and p is the scattering parameter related to the relaxation time τ by

$$\tau = \tau_0 E^p$$

with $p = -1/2$ (acoustic phonons), $p = 1/2$ (optical phonons), $p = 3/2$ (ionized impurities) or $p = 0$ (neutral impurities). Taking into account the expression for the Fermi energy in a degenerate semiconductor, from eqn. (1) one can obtain

$$\alpha_e = \frac{2\pi^{3/2} k^2 m^* (1/2 + p/3) T}{|e| \hbar^2 (3n)^{2/3}} \tag{2}$$

From the experimental points as in Fig. 5 a constant A in the relation

$$m^* (1/2 + p/3) = A n^{2/3} \tag{3}$$

can be determined. Therefore it is possible to calculate the effective mass m^* for a given carrier concentration n and scattering parameter p .

Comparing the calculated effective masses (Table II) with those obtained from

TABLE II
EFFECTIVE MASSES m^* IN RELATION TO THE FREE-ELECTRON MASS m_e CALCULATED FROM EQN. (3) FOR THE DATA SHOWN IN FIG. 5

	m^*/m_e for the following values of p			
	$-1/2$	0	$1/2$	$3/2$
Cd ₂ SnO ₄	0.50	0.33	0.25	0.17
CdIn ₂ O ₄	0.74	0.49	0.37	0.25

the optical measurements (see Section 5), one can draw the conclusion that for the CdIn_2O_4 sample the most probable value of the parameter p is $3/2$, i.e. the scattering at ionized impurities dominates. However, for Cd_2SnO_4 films it is impossible to determine from TEP measurements which type of scattering prevails.

5. OPTICAL PROPERTIES

The optical transmission T and reflection R for Cd_2SnO_4 and CdIn_2O_4 films were measured in the wavelength range from 0.3 to 10 μm using Zeiss UV-visible and Zeiss IR double-beam spectrophotometers. Typical transmission and reflection spectra for CdIn_2O_4 films with a high concentration of charge carriers are shown in Fig. 6.

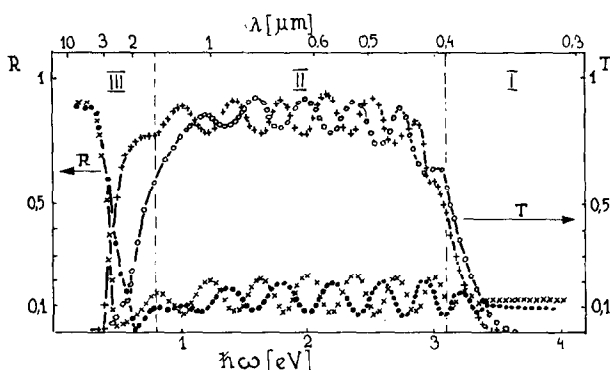


Fig. 6. Optical transmission T and reflection R spectra for CdIn_2O_4 films with electron concentrations $n = 1.8 \times 10^{26} \text{ m}^{-3}$ (+, \times) and $n = 3.2 \times 10^{26} \text{ m}^{-3}$ (O, \bullet).

The spectrum in Fig. 6 can be divided into three regions: the region of the fundamental absorption edge (I), the region of weak absorption (II) and the region of the plasma reflection edge (III). For films with a low carrier concentration the plasma reflection edge is not observed. Optical spectra for Cd_2SnO_4 thin films are similar to those recorded^{5,11} for CdIn_2O_4 .

The spectral region of plasma reflection was discussed in detail in our previous paper¹³. The effective masses m^* of conduction electrons determined in this region are small and increase with an increase in electron concentration:

$$\text{Cd}_2\text{SnO}_4 \quad m^* = (0.18-0.55)m_e$$

$$\text{CdIn}_2\text{O}_4 \quad m^* = (0.24-0.34)m_e$$

Calculations of the optical constants, i.e. the absorption coefficient and refractive index, in the region of weak absorption were performed using a model of an optically inhomogeneous layer on a non-absorbing substrate^{15,16} (Fig. 7). The surface roughness that affects the measured values of optical parameters was also taken into account (Fig. 8).

Utilizing a special numerical procedure¹⁷ it was possible to calculate the refractive index n_z at the air-to-film interface, the refractive index n_w at the film-to-

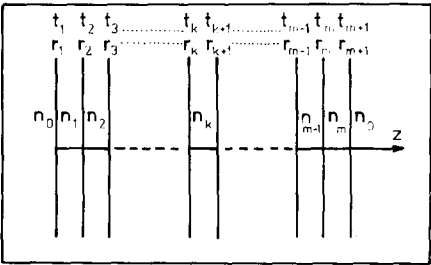


Fig. 7. Optically inhomogeneous film as a pile of m homogeneous layers: n_0 is the refractive index of the ambient medium.

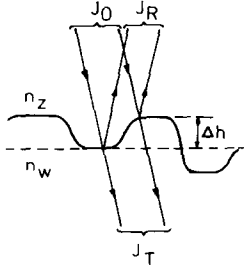


Fig. 8. The air-to-film interface: n_z and n_w are the refractive indices at air-to-film and film-to-surface interfaces respectively; $S = 2\pi \Delta h$; Δh is the amplitude of the surface irregularities.

substrate interface, the product of the absorption coefficient and the film thickness as well as the parameter S which describes the roughness of the film surface.

The spectral dependence of n_z and n_w is presented in Fig 9. The refractive index at the film-to-substrate interface is not affected by the composition of the reactive $\text{Ar} + \text{O}_2$ gas mixture during sputtering. However, the refractive index at the air-to-film interface decreases with a decrease in oxygen concentration.

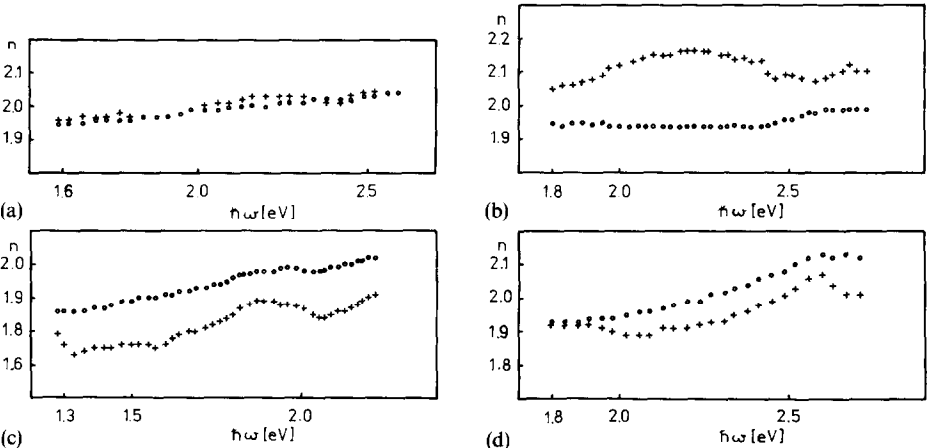


Fig. 9. Spectral dependence of the refractive indices n_z (+) and n_w (O) for CdIn_2O_4 films prepared as follows: (a) "as sputtered" at 100% O_2 ; (b) sample as in (a) after reduction at 670 K; (c) "as sputtered" at 7% O_2 ; (d) sample as in (c) after reduction at 670 K.

The approximate analysis^{10,17} performed in the region of the fundamental absorption edge enabled the evaluation of the optical band gap for both kinds of films:

$$\begin{array}{ll} \text{Cd}_2\text{SnO}_4 & E_{\text{opt}} = 2.35\text{--}3.00 \text{ eV} \\ \text{CdIn}_2\text{O}_4 & E_{\text{opt}} = 2.67\text{--}3.24 \text{ eV} \end{array}$$

The optical band gap increases with the increase in the electron concentration, which can be explained in terms of the Burstein shift¹⁸.

6. CONCLUSIONS

Hall and TEP measurements indicate that Cd_2SnO_4 and CdIn_2O_4 thin films prepared by d.c. reactive sputtering from metallic alloy targets are in general in a state of degeneracy even without intentional doping. Post-deposition heat treatment in vacuum or in a reducing atmosphere leads to an increase in the degree of degeneracy. Hence electrical conductivities as high as $10^5 \Omega^{-1} \text{m}^{-1}$ may be easily attained.

The process of electron scattering is mostly due to charged point defects.

Optical transmission in the visible region of the light spectrum is sufficiently large (75%–80% for Cd_2SnO_4 and 85%–90% for CdIn_2O_4) to enable these films to be considered as highly promising candidates for transparent electrodes.

ACKNOWLEDGMENT

Dr. K. Zakrzewska would like to acknowledge the support of Professor Elsa Garmire, Director of the Center for Laser Studies.

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