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ELECTRICAL AND OPTICAL PROPERTIES OF CONDUCTING N-TYPE Cd_2SnO_4 THIN FILMS*

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Polycrystalline Cd_2SnO_4 thin films were prepared by d.c. reactive sputtering from Cd–Sn alloy targets. X-ray spectroscopy revealed that the tin cations occupy the octahedral sites in a spinel structure. Mössbauer measurements confirmed this result. Measurements of the electron concentration, the mobility and the thermoelectric power as functions of the temperature revealed that the films were degenerate semiconductors. The electrical properties of the films after post-deposition heat treatment in oxygen indicated the origin of the free carriers and the nature of the scattering process. The fundamental absorption edge showed a Burstein shift. The electron effective mass was calculated from the IR plasma reflection.

1. INTRODUCTION

Because of their high transparency in the visible region (80%–90%) and high conductivity (sheet resistance, 1–50 Ω/□) Cd_2SnO_4 thin films, like the already used SnO_2:Sb and In_2O_3:Sn coatings, are being exploited for optoelectronics and solar energy conversion devices[1–5]. D.c. sputtering is a useful method of obtaining these films on a large scale.

2. FILM PREPARATION

Cd_2SnO_4 thin films were prepared by d.c. reactive sputtering from 66%Cd–34%Sn alloy targets (purity, 99.999%). The spacing of the target to the substrate (Corning 7059 glass) was 35 mm, the total pressure was 6 Pa and the discharge voltage was 2000 V. The discharge was carried out in a chamber in Ar–O_2 gas mixtures with various oxygen concentrations. The substrate temperature was about 650 K and the deposition time was 30–100 min. Some films (obtained under the same conditions) were heat treated after deposition for 1 h in oxygen at 673 K and at a pressure in the range from 133 to 1.33×10^{-2} Pa.

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3. FILM STRUCTURE AND MÖSSBAUER MEASUREMENTS

The structural investigations were performed using electron microscopy and X-ray diffractometry. The Cd_2SnO_4 films were polycrystalline with a grain size of about 500 Å and they crystallized in the inverse spinel structure (space group, $Fd\bar{3}m\,(O_h^7)$; Fig. 1) with a cell lattice parameter $a = 9.172$ Å and an oxygen parameter $u = 0.384$ Å. Half of the cadmium cations occupy tetrahedral sites and the remaining cadmium cations are distributed with the tin cations on the octahedral sites ($Cd[Sn\,Cd]O_4$). The films exhibited a texture along the [100] direction perpendicular to the substrate.

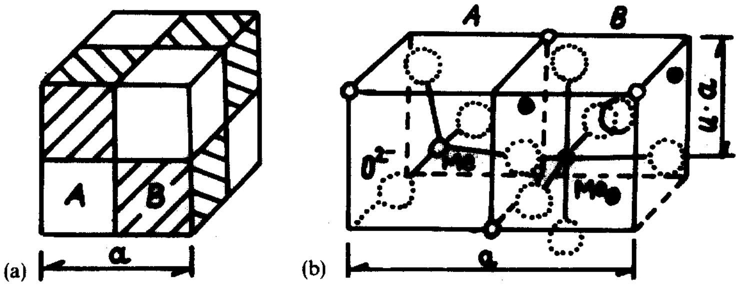


Fig. 1. (a) Representation of the unit cell of the spinel structure in the form of blocks. It has been found that each of the four curves (shaded and unshaded) has an identical ionic structure which is shown in (b). The oxygen parameter u indicated in (b) is defined as the distance between the oxygen ions and the crystal edge. In an ideal case $u = 3/8$.

The Mössbauer effect was used to study the oxidation states and site distribution of tin in the spinel. The ^{119}Sn Mössbauer spectra were recorded at room temperature using the transmission technique with a barium stannate source. They consist of quadrupole doublets with a small splitting. The investigations confirmed that Cd_2SnO_4 is a compound of tetravalent tin. There is no contribution from divalent tin. The fitted spectral parameters, namely the isomer shifts IS, the quadrupole splittings QS and the linewidth Γ, had values in the range 0.22–0.253 mm s^{-1} relative to SnO_2, 0.56–0.742 mm s^{-1} and 0.881–0.933 mm s^{-1} respectively. These values depended on the oxygen content in the films. Cd_2SnO_4 is not a fully ionic tin compound.

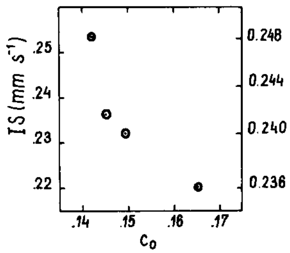
Applying the formula of Lees and Flinn[6] the number n_s of 5s electrons in tin can be calculated from the IS. IS and n_s decrease with increasing oxygen content (Fig. 2). The oxygen mass content was measured using an electron microprobe. The electron concentration also decreased with either increasing oxygen content or increasing oxygen pressure (see eqn. (5)).

Quadrupole splitting did not vanish for the films investigated. This is caused by the non-zero electric field gradient at the cation resulting from the non-cubic symmetry of the octahedral sites.

4. ELECTRICAL MEASUREMENTS

Conductivity, Hall[7] and thermoelectric power (TEP) measurements were carried out in the temperature range 77–400 K (magnetic field $B = 1$ T).

The films obtained using a gas mixture containing 60% O_2 exhibited a high electron concentration which varied from 7×10^{25} to 3×10^{26} m^{-3} depending on heat treatment conditions and which remained nearly constant over the range of measurement temperatures investigated. The TEP increases with increasing temperature (Fig. 3). Such behaviour of the electron concentration and the TEP indicates that Cd_2SnO_4 is a degenerate semiconductor.



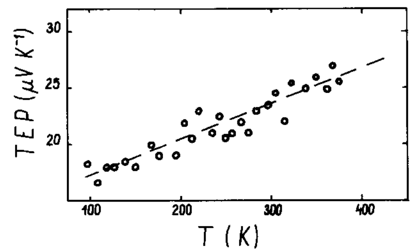


Fig. 2. Isomer shift IS and number n_s of 5s electrons *vs.* the oxygen content c_O.

Fig. 3. Temperature dependence of the TEP for a Cd_2SnO_4 film.

After the sputtering the films were heat treated in the same sputtering chamber. The chamber was evacuated and then the films were heated at 673 K for 1 h in an atmosphere of O_2 at an appropriate pressure P_{O_2}. Such treatment led to variations in the carrier concentration N. N decreased with increasing oxygen pressure and the variation could be fitted to a power law:

$$N \propto P_{O_2}{}^{-1/\alpha} \tag{1}$$

where $\alpha = 7.8$. The reaction proposed earlier[7] which permits the existence of interstitial ionized cadmium $Cd_i^{\cdot}$ and oxygen vacancies $V_O^{\cdot\cdot}$ as the point defects is

$$2Cd_{Cd}{}^{\times} + Sn_{Sn}{}^{\times} + 4O_O{}^{\times} \rightleftharpoons 2Cd_i^{\cdot} + Sn_{Sn}{}^{\times} + 4V_O^{\cdot\cdot} + 10e' + 2O_2(g) \tag{2}$$

where $Cd_{Cd}{}^{\times}$, $Sn_{Sn}{}^{\times}$ and $O_O{}^{\times}$ are cadmium, tin and oxygen in lattice sites respectively and $O_2(g)$ is oxygen in the gas phase. Use of the law of mass action[8] with the electroneutrality condition

$$N = 2[V_O^{\cdot\cdot}] + [Cd_i^{\cdot}] \tag{3}$$

where $[V_O^{\cdot\cdot}]$ and $[Cd_i^{\cdot}]$ are the concentrations of defects, together with the assumption that

$$[V_O^{\cdot\cdot}] = [Cd_i^{\cdot}] \tag{4}$$

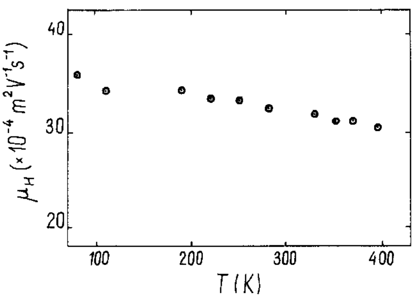
yields

$$N \propto P_{O_2}{}^{-1/8} \tag{5}$$

The temperature dependence of the Hall mobility indicates that the scattering of charged carriers by point defects is dominant in Cd_2SnO_4 (Fig. 4). The postulated point defects are oxygen vacancies, interstitial cadmium ions and neutral complexes $(CdO)^{\times}$

5. OPTICAL PROPERTIES

The optical transmission of the films was measured as a function of the photon energy from 0.48 to 3.5 eV using a double-beam spectrophotometer. Typical transmission and reflection spectra are shown in Fig. 5.



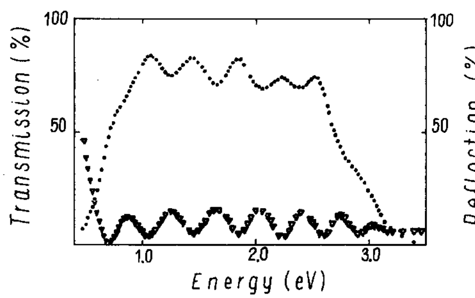


Fig. 4. Temperature dependence of the Hall mobility μ_H for a Cd_2SnO_4 film of electron concentration $N = 2.8 \times 10^{26}\ m^{-3}$.

Fig. 5. Transmission T and reflection R *vs.* the photon energy.

The shifts in the fundamental optical absorption edge towards higher energy with increasing electron concentration can be interpreted as a Burstein effect[9]. The observed maximum value of the optical gap was 3.04 eV.

Use of the McLean method of analysis[10] indicates the existence of direct forbidden transitions and the absorption curve can be described by the formula

$$\alpha h\nu = A(h\nu - E_g)^{3/2} \tag{6}$$

All the films were reflective in the IR region and the observed minimum of the reflectivity lay in the energy range 0.55–0.72 eV depending on the electron concentration of the samples. The effective mass m^* calculated from the equation

$$\omega_{plas}{}^2 = \frac{Ne^2}{m^* \varepsilon_0 \varepsilon_\infty} \tag{7}$$

where ε_∞ is the high frequency dielectric constant and is 4.2 for Cd_2SnO_4 thin films, is about 0.25 times the electron mass.

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