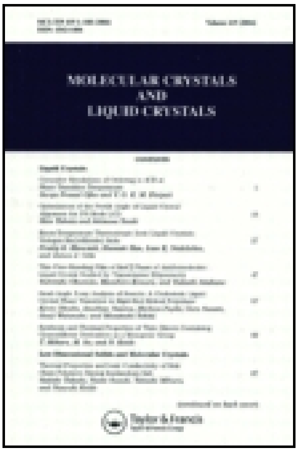

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A Study on the Formation of a Porous Morphology in Cd 2 SnO 4 Thin Films Prepared by Mod Process

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A Study on the Formation of a Porous Morphology in Cd_2SnO_4 Thin Films Prepared by Mod Process

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Transparent and conductive Cd_2SnO_4 films were prepared by Metallorganic Decomposition technique. Cadmium and tin 2-ethylhexanoates were dissolved in xylene and 2-ethylhexanoic acid, respectively, and the solution formed was used as precursor. The films were deposited by dip coating on borosilicate glass and quartz, and annealed at 600 and 620°C. Films with high uniformity, thickness of 350 nm, optical transmission higher than 92% ($Eg \sim 3.06$ eV), and resistivity c.a. 10^{-3} Ω.cm were obtained. The nature of solvent is important to control the film morphologies.

Keywords: Cd_2SnO_4; transparent conducting films; MOD; Metallorganic Decomposition

INTRODUCTION

Cd_2SnO_4 shows an interesting and technologically important combination of properties: it exhibits high optical transparency, high infrared reflectance, and good electrical conductivity. This material belongs to a unique class known as TCOs (transparent conducting oxides). Since the 60's, the most used TCO for optoelectronic device applications has been tin-doped indium oxide (ITO) [1]. Although binary compounds like SnO_2 and ZnO_2 have been used in such applications, Cd_2SnO_4 presents superior electrical and optical properties [2].

Among the most important applications of TCOs, it is worth to mention they are used in the larger flat-screen high-definition televisions (HDTVs), the larger and higher-resolution screens of portable computers, electrochromic windows, and photovoltaic thin films [3]. Herein, it is reported the fabrication of Cd_2SnO_4 thin films by Metallorganic Decomposition (MOD). MOD technique is a very promising synthetic route to multicomponent film preparation [4, 5].

EXPERIMENTAL

Xylene solutions of cadmium 2-ethylhexanoate ($Cd(hex)_2$) and tin 2-ethylhexanoate ($Sn(hex)_2$) were used in deposition experiments by dip coating technique on sodium borosilicate glass and quartz substrates. Solution concentrations (0.25 mol L^{-1} $Cd(hex)_2$, 0.14 mol L^{-1} $Sn(hex)_2$ and 0.39 mol L^{-1} $Cd(hex)_2$, 0.20 mol L^{-1} $Sn(hex)_2$), withdrawal rate (2 cm min^{-1} and 5 cm min^{-1}), pyrolysis temperature (400°C and 430°C), and heating rate (5°C min^{-1} and 10°C min^{-1}) were the variables investigated by 2^4 factorial design. Annealing treatments were performed at 600°C/11h and 620°C/5h. Evaluation of solvent effects on film morphologies was carried out switching from xylene to 2-ethylhexanoic acid for the most concentrated solution.

The films were characterized by X-ray diffractometry (Shimadzu XRD-6000, CuKα, λ = 1.5418 Å), Raman microspectroscopy (Renishaw U-300 spectrometer with a 632.8 nm He-Ne laser, coupled to an Olympus microscope and CCD detector), Field Emission Scanning Electron Microscopy (Jeol, JSM-6340F), and UV-Vis-NIR absorption spectroscopy (Varian UV-Vis-NIR spectrophotometer Cary 5G). Film thickness and electrical resistance were measured by rugosimetry (Alpha Step 200), and by four-point probe method, respectively.

RESULTS AND DISCUSSION

Cubic spinel structure Fd3m was observed for the Cd_2SnO_4 films deposited on both glass (borosilicate) and quartz substrates heated at 600 and 620°C, respectively (Figure 1) [6]. Although this structure is unstable in bulk form, it is readily observed in films. In such case, the bulk phase diagrams cannot account for the range of metastable phase in the films obtained. This result could be explain due to an interface interaction between film and SiO_2 of substrate, since cubic structure was formed on both glass and quartz.

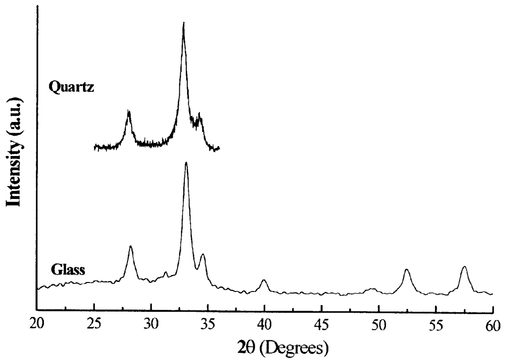

FIGURE 1: X-ray diffraction of Cd_2SnO_4 films obtained on glass and quartz substrates.

Raman spectrum of a Cd_2SnO_4 film on glass shows a strong band at 637 cm^{-1} and a weak band at 492 cm^{-1}, assigned to the ν_s and ν_{ass} modes of the Sn-O bonds, respectively (Figure 2).

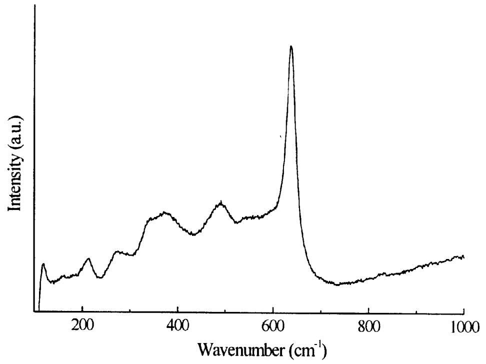

FIGURE 2: Raman spectrum of the Cd_2SnO_4 film.

All films prepared according to the 2^4 factorial design were transparent. However, when the lowest precursor concentration, withdrawal rate of 2 cm min^{-1}, heating rate of 10°C min^{-1}, pyrolysis temperature of 400°C were used, films with thickness of 350 nm (± 10 nm), transmittance higher than 92% over the 500 - 2000 nm range were obtained (Figure 3) The transition observed at 297 nm can be assigned to Sn-O CT transition.

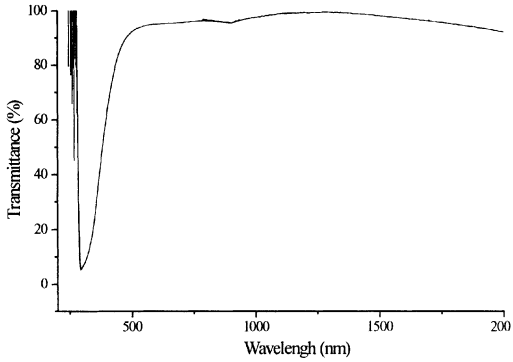

FIGURE 3: Optical transmission of Cd_2SnO_4 film on glass.

The value of optical band gap of Cd_2SnO_4, derived from the absorption data, was 3.06 eV. It was observed a large shift of the fundamental optical absorption edges towards shorter wavelengths depending on the preparation variables. The maximum optical gap induced by the Moss-Burstein effect in Cd_2SnO_4 films was 3.40 eV. The Moss-Burstein shift is a function of both the carrier density and the effective mass of the conduction electron ($\Delta E_{MB} \propto n^{2/3}/m^*$, n is the carrier density and m^* is the effective mass of electron) [7, 8]. Therefore, the shift in the Fermi level with reference to the conduction band minimum is related with either increase of carrier density or decrease of effective mass.

The resistivity was 4.02×10^{-3} Ω cm for the film with 92% of transmittance. This resistivity is higher than reported value for Cd_2SnO_4 film prepared by sputtering [9]. Probably the resistivity is affected by the porous morphology, Figure 4 (A).

The pore formations were studied taking in to account the evolution of the film morphology. Dendritic morphologies were obtained after both the solvent evaporation at 150°C, from a single layer of concentrated precursor solution deposited on the substrate, and the single pyrolysis step (Figure 4 B and C). This result indicates that the film morphology evolves from a dendritic form, for a single layer, to a porous structure as more layers are deposited. Dendritic habits result when growth becomes limited by one of its constituent transport processes. The change from nucleation controlled to diffusion controlled (dendritic) growth is susceptible to many variables such as solvent nature, crystallization temperature, and precursor concentration.

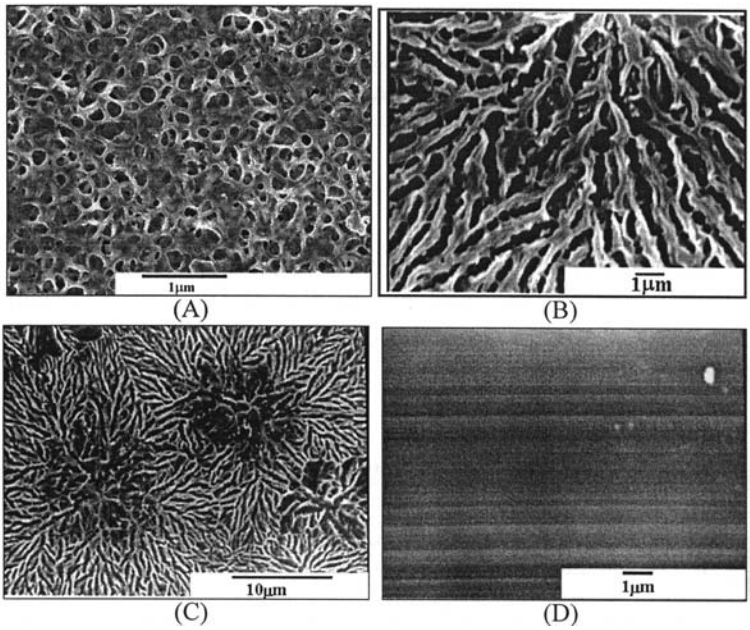

FIGURE 4: SEM micrograph of Cd_2SnO_4: (A) annealed at 600°C and 620°C using xylene as solvent; (B) one layer of $Cd(hex)_2$ and $Sn(hex)_2$ precursors (150°C); (C) one layer of $Cd(hex)_2$ and $Sn(hex)_2$ precursors after pyrolysis step at 400°C; and (D) annealed at 600°C and 620°C using 2-ethylhexanoic acid as solvent.

Evaluation of solvent effects on film morphology was carried by out switching from xylene to 2-ethylhexanoic acid as solvent of the most concentrated solution. Resulting films were smoothes and denses after ten depositions and annealing on borosilicate substrate at 600°C and 620°C (Figure 4 D). Concerning the Cd_2SnO_4 films, the nature of the solvent controls their morphologies. Cubic spinel structures of Cd_2SnO_4 were observed for the films prepared using 2-ethylhexanoic acid as solvent.

CONCLUSIONS

Homogenous and uniform semiconductor Cd_2SnO_4 thin films were successfully prepared by Metallorganic Decomposition technique. The advantages of film preparations by the MOD technology include low-temperature processing of single-phase spinel Cd_2SnO_4, transmittance higher than 92%, morphology modulated by the nature of the solvent, and possibility to produce transparent and conductive thin films.

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