

Structural and Surface Morphology of Multi-phase Cadmium Stannic Oxide Thin Films Prepared by Spray Pyrolysis Technique

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Abstract: In this study, cadmium stannic oxide (Cd-Sn-O) (CSO) thin films of different Sn mole fractions ($\text{Sn}/(\text{Sn}+\text{Cd})$) were prepared by spray pyrolysis. X-ray diffraction measurements showed polycrystalline structures of Cd_2SnO_4 phase and minor phases of CdSnO_3 and SnO_2 at 0.1 Sn ratio. Increasing the Sn concentration caused reducing the polycrystalline structure phase of Cd_2SnO_4 and increasing CdSnO_3 being the dominant phase at 0.3 Sn mole fraction. The polycrystalline structure phase of SnO_2 appeared as dominant at 0.5 Sn mole fraction. Field Emission Scanning Electron Microscopy (FE-SEM) was employed to investigate CSO that was prepared at different Sn mole fractions. The FE-SEM results of CSO thin films at 0.1 mole fraction showed nanorods which are 266 nm in diameter and the dimensions of the observed nanorods showed maximum at 0.2 Sn mole fraction. The sample prepared with 0.3 Sn mole fraction appeared as two particle structures; small spherical structures with a diameter of 250 nm attached to each other covered by radially branched laminate structures on the film surface. These shapes were about 470 nm wide and 3.5 μm long. In the sample type, at 0.4 Sn mole fraction, the lamellar structure emerged to curl and covered a larger area of the film surface. At the ratio of 0.5, the lamellar structure covered the entire surface of the film.

Keywords: Cadmium stannic oxide, Metal oxide, (Cd, Sn) oxide composite, Spray pyrolysis.

1. Introduction

Transparent conductive oxides (TCOs) have many applications, such as liquid-crystal displays, OLEDs, touchscreens and photovoltaics, based on their distinct photoelectric properties [1]. One of the most popular TCOs is indium tin oxide (ITO), but due to its high cost, high efforts have been made to discover and develop alternatives to this material. Cd_2SnO_4 spinel thin films have a high electrical conductivity and a low absorbency to visible light [2]. Studying the structural, electronic and optical properties of ternary Cd-Sn-O phases, such as spinel Cd_2SnO_4 [3] and

ilmenite or perovskite CdSnO_3 [4], has received high attention. The cadmium stannate (Cd_2SnO_4) can exist in cubic (at low temperatures) and orthorhombic (at high temperatures) crystalline structures [5]. Cd_2SnO_4 has been produced by using numerous techniques, such as thermal reaction [5], rf sputtering [1], hydrothermal [6], Sol-gel [7] ... etc. Thin films of the cubic spinel Cd_2SnO_4 phase are known to have high electron mobility and electrical conductivity, in addition to high transparency of visible light [8]. These properties make Cd_2SnO_4 fit for many applications, such as in transparent conducting

oxides in thin-film devices [9], solar water splitting [10] and gas-sensing applications [11].

The other ternary compound in this study is CdSnO_3 , which exhibits a crystalline form as rhombohedral ilmenite-structure, of lattice constants $a = b = 5.452 \text{ \AA}$, $c = 14.947 \text{ \AA}$ [12] or as orthorhombic perovskite of lattice constants $a = 5.55 \text{ \AA}$, $b = 5.67 \text{ \AA}$, $c = 8.04 \text{ \AA}$ [10]. It can be prepared by thermal reaction [12], hydrothermal autoclave [13] and chemical spray pyrolysis [14]. It was investigated for gas sensing in different applications, such as chlorine gas sensing [15] and porous micro-cubes for ethanol sensing [12].

The spray pyrolysis technique is a promising method for simply depositing large coating areas. Abrutis et al. (2007) prepared conductive cadmium stannate (Cd_2SnO_4) films by the spray-pyrolysis technique at a deposition temperature of $400 \text{ }^\circ\text{C}$ or below. Typical resistivity values of Cd_2SnO_4 films were found to be $\sim 2 \times 10^{-3} \text{ } \Omega \cdot \text{cm}$ [16]. Rivera et al. (2018) deposited Cd_2SnO_4 by the same technique from tin chloride and cadmium acetate solution in water/isopropanol (4:1) mixture, at an atomic ratio of $\text{Cd}/\text{Sn} = 6$. The substrate temperature was varied in the range of $410\text{--}500 \text{ }^\circ\text{C}$. The crystallinity was improved by rapid thermal annealing at $600 \text{ }^\circ\text{C}$, under two different atmospheres of argon and vacuum [17].

Due to the lack of information about the ternary phases of Cd-Sn-O prepared by spray pyrolysis, the temperature of crystallization and the proportions of molar ratios for the different phases were studied in this work. Starting with aqueous solutions of CdCl_2 and $\text{SnCl}_4 \cdot 5\text{H}_2\text{O}$, the Cd-Sn oxide thin films were prepared at different atomic ratios of Cd:Sn. The structural properties, phases' ratio, surface morphology and element analysis of the prepared films were studied to find out the effect of the substrate temperature and the molar fraction on the obtained polycrystallinity phases in this system.

2. Experimental

Mixed phases of cadmium stannic oxide (Cd-Sn-O) thin films of different Cd/Sn atomic ratios were prepared by spray pyrolysis from the stannic chloride (SnCl_4) of 99.999% purity and cadmium chloride (CdCl_2) of 99.995% purity, purchased from (Sigma-Aldrich Co.) without any further purification. A solution of the two

powders was prepared in distilled water with 0.1 M at different molar ratios. The solution was homogenized and mixed at room temperature using a magnetic stirrer until attaining a clear solution. The films were deposited on glass slides by the simple spray pyrolysis technique onto a controlled temperature hot plate at $500 \text{ }^\circ\text{C}$. The atomizer was at a vertical height of 30 cm from the substrates. The aqueous solution was sprayed by employing compressed air of 4 bar pressure at a flow rate of 2 ml/min. The prepared films on the substrates were kept after ending the spray process for 30 minutes at the same temperature ($500 \text{ }^\circ\text{C}$). Finally, the substrates were cooled down gradually (20 degrees/min) until reaching room temperature.

The structural properties and surface morphology of the prepared thin films at different molar ratios were measured by x-ray diffraction (Shimadzu 6000-XRD) at an angle range of ($20\text{--}80 \text{ degrees}$) using a Cu K_α source of wavelength 0.15406 nm and field emission scanning electron microscopy (JSM-7600F by JEOL, Ltd.). 2D XRD characterizations, by X Powder software (Ver. 2004.04.70 PRO) package, was used to identify the points of phase transitions in Cd-Sn-O composite thin films deposited on glass substrates at different molar ratios. The film thicknesses were measured using (TFProbe TM from Angstrom Sun Technology, Inc.) and were found to be about $250 \pm 10 \text{ nm}$ for all films.

3. Results and Discussion

Identification of the polycrystalline structure phases of the CSO composite was determined by XRD. Fig. 1 demonstrates the diffraction patterns of the thin films at different Sn molar fractions (0.1, 0.2, 0.3, 0.4 and 0.5) prepared by spray pyrolysis on glass slides at $500 \text{ }^\circ\text{C}$ substrate temperature. The modulation hump at around 24° is corresponding to the glass substrate. Polycrystalline structures emerged in all samples, starting with the major phase of Cd_2SnO_4 at the lowest Sn ratio and a broad peak at around 30° matched with the (104) plane for the CdSnO_3 phase. Increasing the Sn ratio causes a reduction in the Cd_2SnO_4 crystallinity till it nearly vanished at 0.5 Sn ratio. The CdSnO_3 structure was enhanced by increasing the Sn ratio to 0.4 and reducing it to 0.5. The dominant phase at 0.1 Sn ratio is the spinel Cd_2SnO_4 and the dominant phase at 0.4 is the orthorhombic

CdSnO_3 phase, while the main phase at 0.5 is the SnO_2 phase. The appearance of any definite Cd-Sn-O ternary phase depends on the atomic Sn/(Sn+Cd) ratio. The presence of Cd_2SnO_4 and CdSnO_3 is more prominent in the case of films containing a relatively low Sn content. On the

other hand, the tetragonal SnO_2 phase is more obvious in samples containing a greater than 0.3 ratio. The SnO_2 phase appeared with broad peaks, indicating that its nanostructure is limited in dimension along the (110) direction.

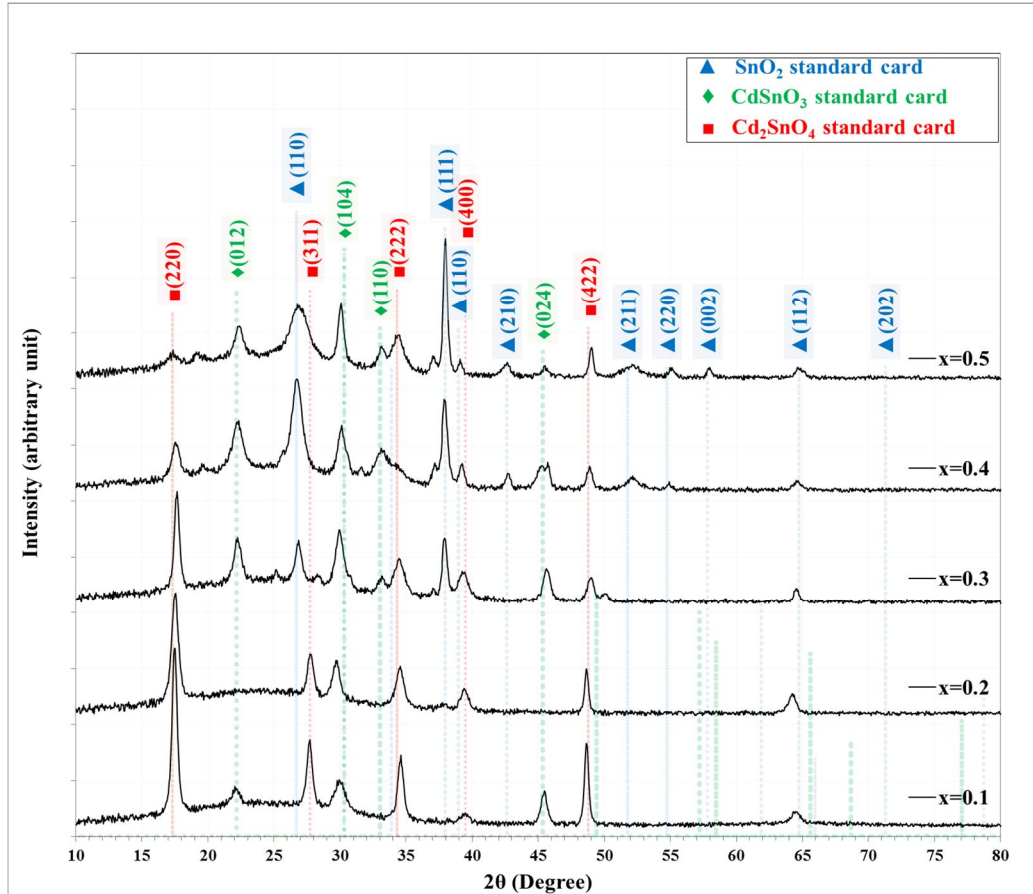


FIG. 1. XRD of the prepared CSO composite thin films at different Sn molar fractions.

Fig. 2 shows the two-dimensional X-ray (2D XRD) analysis using X Powder software (Ver. 2004.04.70 PRO) package, which shows that the Cd_2SnO_4 structural phase is the predominant phase for the samples prepared from 0.1 to 0.3 Sn molar fractions. The predominant structural phase at 0.4 Sn molar fraction is CdSnO_3 , while at 0.5 Sn mole fraction, the SnO_2 was the predominant structural phase. There were interference coexisting phases in the samples prepared at different mole fractions; i.e., there are no pure structural phases at any mole fraction.

Fig. 3 shows FE-SEM images, at two different magnifications, of CSO thin films prepared at 0.1 Sn molar fraction deposited on a glass substrate at a substrate temperature of 500 °C. The surface of the prepared films contains

nanorods 266 nm in diameter and several micrometres in length emerging on the surface.

Fig. 4 shows the FE-SEM images, at two magnifications, of the CSO thin films at 0.2 Sn mole fraction. The morphological structure emerged on the surface gradually.

Fig. 5 shows the FE-SEM images, at two magnifications, of the CSO thin films prepared at 0.3 Sn mole fraction. Two morphological structural modes emerged: spherical structures of 250 nm diameter attached with each other forming the main body of the sample surface; on the top of those, radially laminate structures branching from central points emerged. The structures are in a combined sheet form with a large surface area compared to the first form. These two structure modes are distributed randomly. Their width is around 470 nm and their length is around 3.5 μm .

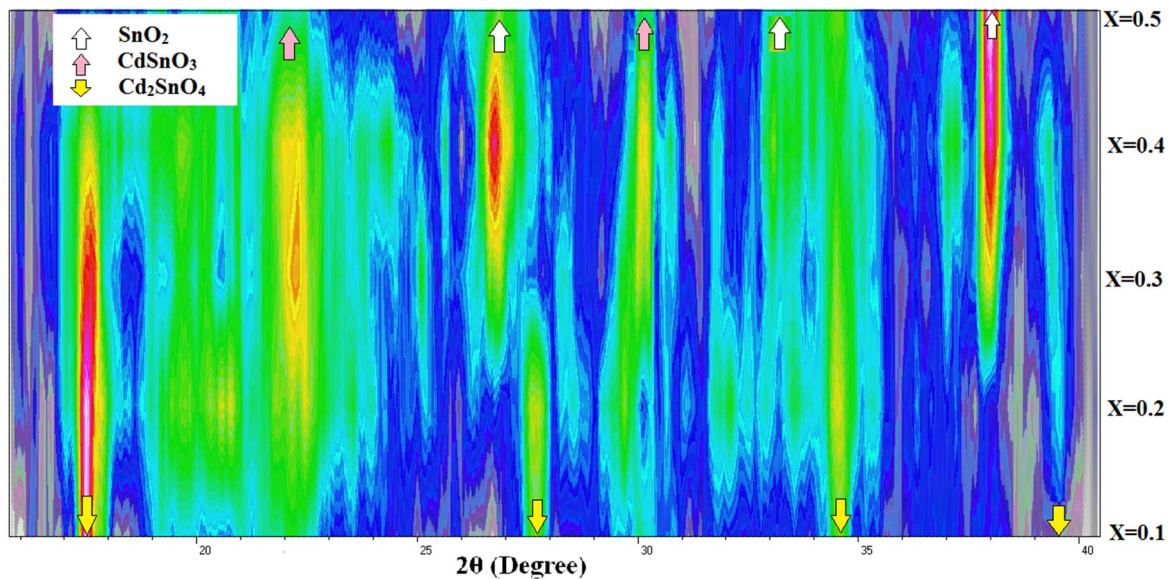


FIG. 2. 2-D XRD spectrum for CSO phase variation with the Sn molar ratio.

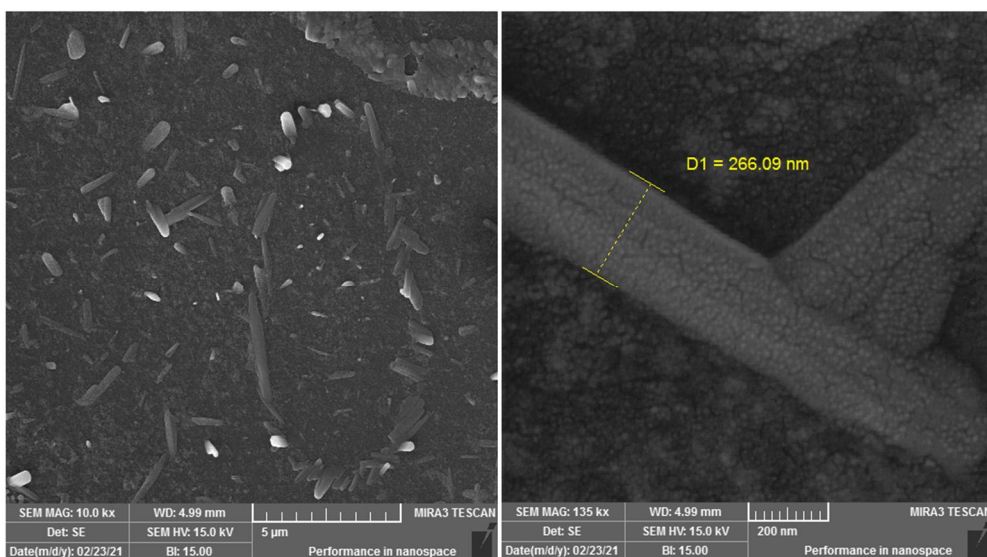


FIG. 3. FE-SEM of CSO nano-structured thin film prepared at 0.1 Sn mole fraction.

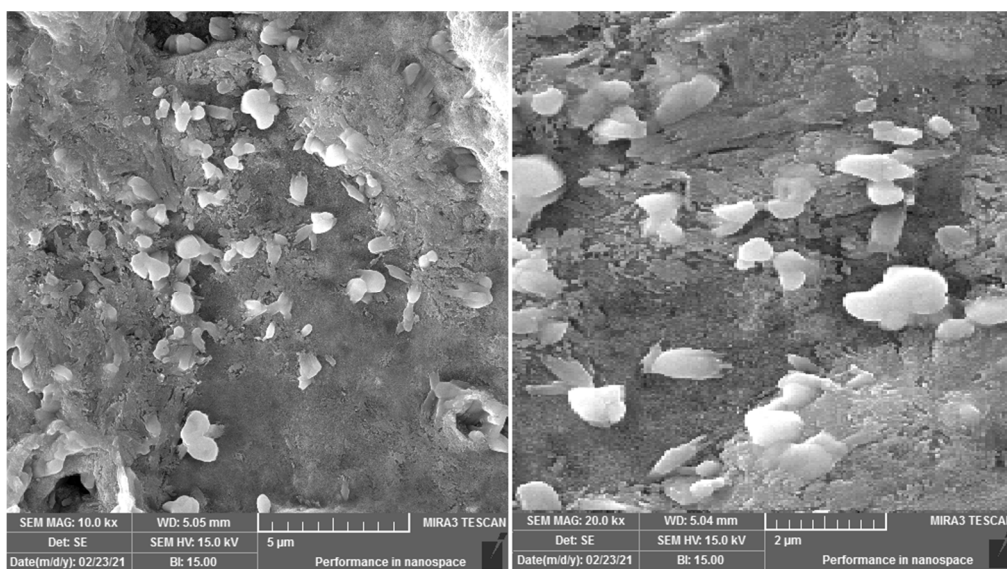


FIG. 4. SEM for CSO nano-structured thin film prepared at 0.2 Sn molar ratio.

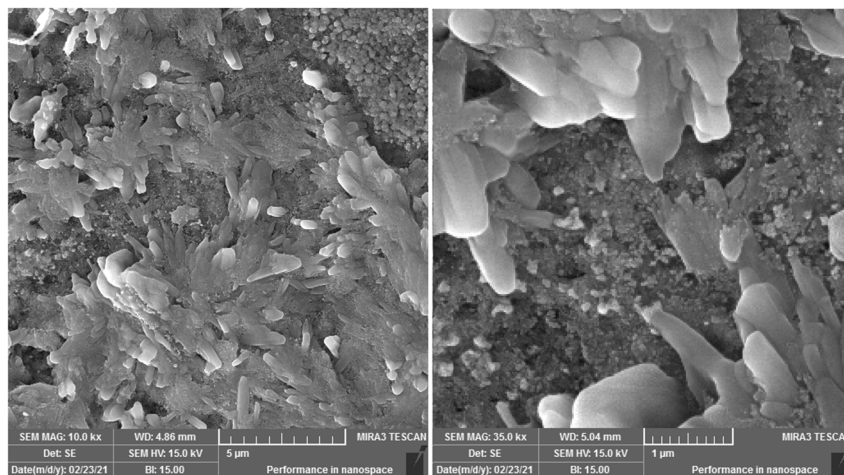


FIG. 5. FE-SEM of CSO thin film prepared at 0.3 Sn molar ratio.

Fig. 6 shows FE-SEM images, with two magnifications, of CSO thin film at 0.4 Sn molar fraction. The lamellar morphological structures emerged, curling to themselves and covering a larger area of the surface compared to the 0.3 mole fraction. Very small shapes in the form of light-coloured dots appeared on the surface of

the sample, with diameters less than 20 nanometers.

Fig. 7 shows the FE-SEM images, with two magnifications, of a thin layer of CSO prepared at 0.5 Sn mole fraction. The lamellar structure covered the entire film surface compared to the case of the previous ratio and is attached to this structure with small spherical shapes.

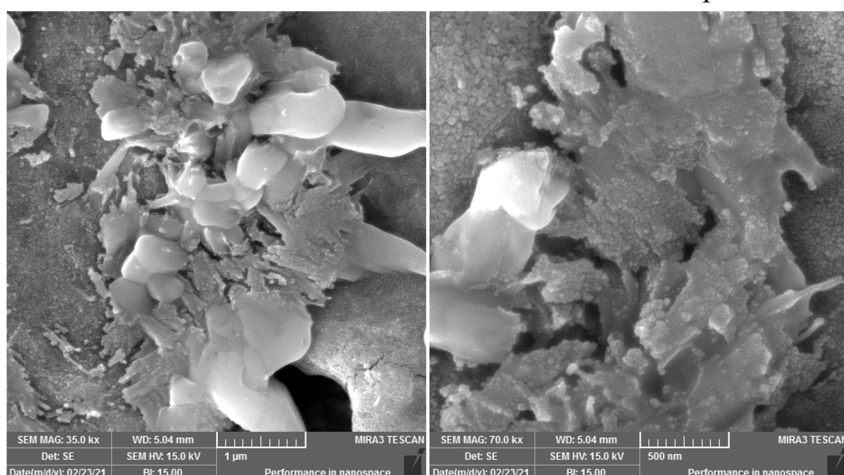


FIG. 6. FE-SEM of CSO thin film prepared at 0.4 Sn mole fraction.

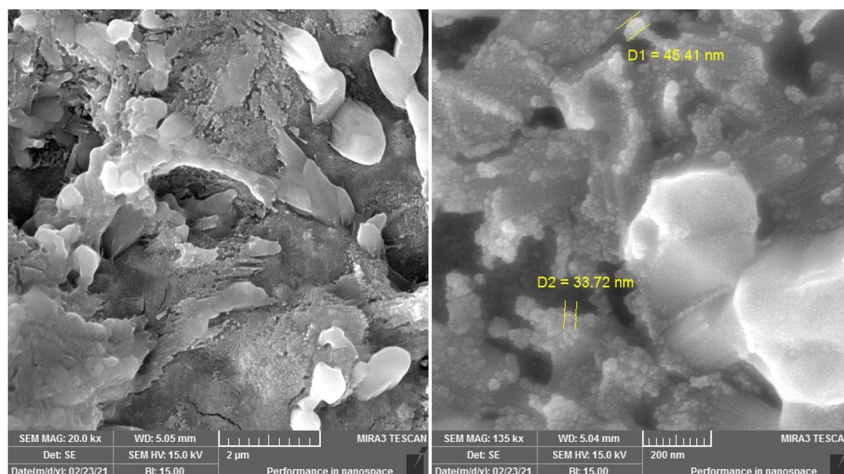


FIG. 7. FE-SEM of CSO thin film prepared at 0.5 Sn mole fraction.

Conclusion

Cadmium stannic oxide (CSO) nanocomposites were prepared by single-step spray pyrolysis at a deposition temperature of 500 °C. 1-D and 2-D XRD results provide evidence of obtaining spinel Cd_2SnO_4 phase at a low mole fraction of Sn at a relatively low temperature, compared to literature. The predominant morphological phase was orthorhombic $CdSnO_3$ and was obtained at 0.3 Sn mole fraction, while the predominant phase was orthorhombic SnO_2 at 0.5 Sn mole fraction. The results of the FE-SEM showed the formation

of morphological nanostructures of various forms depending on the Sn mole fraction, varying from spherical nanostructures to branched plates with a high surface area in addition to nanoparticles attached to their surfaces. The results provide evidence of potentials to modify the final phase of the deposited films as well as the form of the morphological nanostructures, allowing tuning the properties of the films for multiple application purposes.

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