

Study of Cobalt-Doped SnO₂ Thin Films

¹H. Pirmoradi, ²J. Malakootikhah, ³M. Karimipour, ⁴A. Ahmadpour,
⁵N. Shahtahmasebi and ⁶F. Ekhtiary Koshky

¹Department of Chemical Engineering, Nanotechnology Center of Ferdowsi
University of Mashhad, Ferdowsi University of Mashhad, Iran

²Faculty of New Science and Technologies University of Tehran, Tehran, Iran

³Department of Physics, Nanotechnology Center of Ferdowsi University of Mashhad,
School of Basic Science, Ferdowsi University of Mashhad, Vali Asr University, Rafsanjan, Iran

⁴Department of Chemical Engineering, Nanotechnology Center of Ferdowsi
University of Mashhad, Ferdowsi University of Mashhad, Iran

⁵Department of Physics, Nanotechnology Center of Ferdowsi University of Mashhad,
School of Basic Science, Ferdowsi University of Mashhad, Iran

⁶East Azarbayjan Power Generation Management Company, Tabriz, Iran

Abstract: In this research, Co-doped SnO₂ thin films were prepared by the spray pyrolysis method using SnCl₄•5H₂O and Co(NO₃)₂ as a precursor and a dopant, respectively. Effects of Fe-doping level (0,2,4,8,10 and 12 mol%) on properties of Co-doped SnO₂ thin films were investigated. The structural and optical properties of thin films were characterized by XRD and UV-Vis techniques. XRD photographs were prepared and show the cassitrite phase formation with tetragonal structure and preferred orientation (110) that may be followed by (101) plane. SEM images show the size distribution of nanoparticles between 10 nm and 100 nm. Absorbance spectra were prepared with spectrophotometer and the band gap of nanoparticles was determined. The results revealed that properties of Co-doped SnO₂ thin films depend on the Co-doping level.

Key words: Cobalt oxide • Tin oxide • Spray pyrolysis • Thin films

INTRODUCTION

Tin dioxide, SnO₂, is an important n-type semiconductor with wide band gap energy ($E_g = 3.6$ eV) [1]. It is well known for its potential technological applications in gas sensors [2-4], transparent conducting electrodes [5], energy storage (e.g. lithium batteries) [6-8], transistors [9] and solar cells [10-11].

Numerous methods have been developed for thin film and nanocrystalline SnO₂ formation. The synthetic approaches include hydrolysis of tin halides or tin alkoxides via sol-gel technique, precipitation, hydrothermal, microemulsion, chemical vapor deposition (CVD), laser ablation, porous anodic alumina templates and so forth. pulse laser deposition (PLD) is the most

common route to prepare thin films among various methods. In recent years, considerable efforts are focused on the synthesis of magnetic impurity-doped SnO₂ thin films in order to explore its diluted magnetic semiconductor (DMS) properties. Chemically stable SnO₂ is an attractive host lattices for the investigation of DMS ferromagnetism.

Coey *et al.* pointed out that the use of thin films should enhance the magnetic properties relative to bulk samples produced by equilibrium processing.

The purpose of the present work was to prepare Co-doped SnO₂ thin films by sol-gel method and to investigate the effects of Co-doping levels on the structural and optical properties of Co-doped SnO₂ thin films.

Table 1: Spray deposition parameters for preparation of Co:SnO₂ films

Carrier gas pressure-air (bar)	Nozzle to substrate distance (cm)	Spray deposition rate (ml/min)	Substrate temperature (°C)	Solution volume (ml)
2.5	40	15	500	30

MATERIALS AND METHODS

The Co-doped SnO₂ films were deposited on glass substrates using a typical spray pyrolysis coating system. The precursor solution was prepared by dissolving a certain amount (0.025 M) of stannic chloride (SnCl₄·5H₂O) and different amounts of cobalt nitrate 6-hydrate (Co(NO₃)₂·6H₂O) in 15 ml of solvent (a mixture of double distilled water and ethanol in a volume ratio of 1:1). The mole percentage of Co(NO₃)₂·6H₂O in solution was changed from 0 to 12 mole%. Before preparation of films, glass substrates were cleaned and placed on the hot plate and in separate spraying process the undoped and Co-doped SnO₂ films were deposited on rotating hot substrates with the conditions mentioned in Table 1.

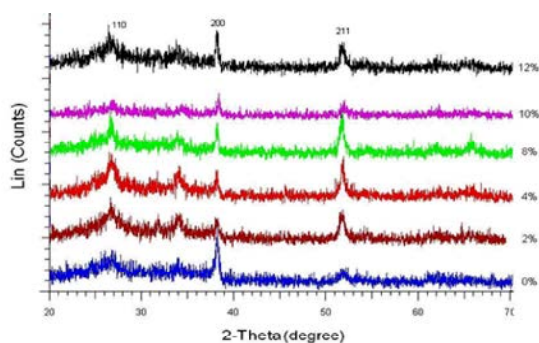


Fig. 1: XRD patterns Co:SnO₂ thin films with different cobalt concentrations

All experiments were done under approximately similar conditions.

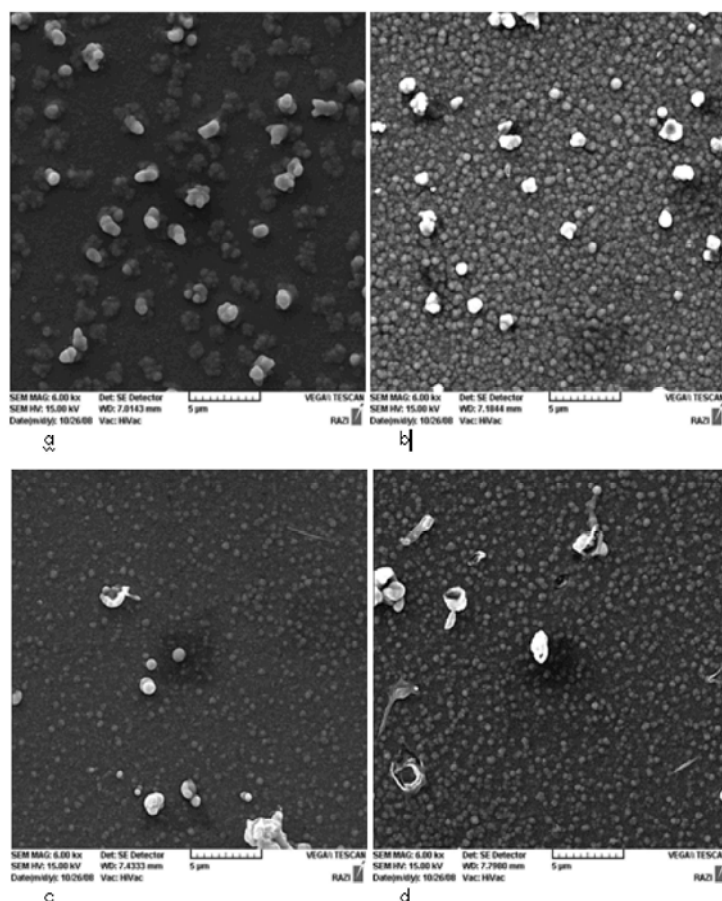


Fig. 2: SEM images of undoped and Co-doped SnO₂ thin films: (a) undoped SnO₂ film, (b) SnO₂:Co (4% mol), (c) SnO₂:Co (8% mol) (d) SnO₂:Co (12% mol)

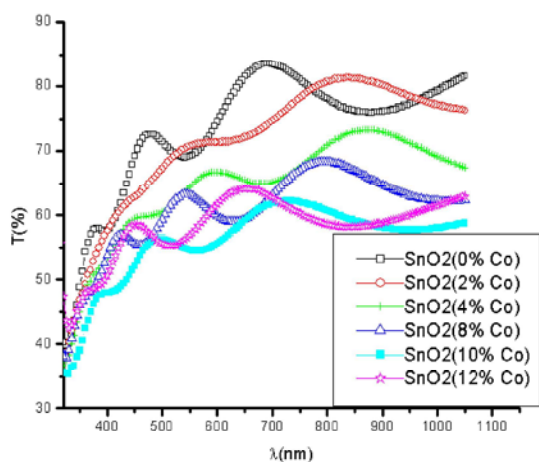


Fig. 3: Optical transparency of various Co-doped SnO_2 films

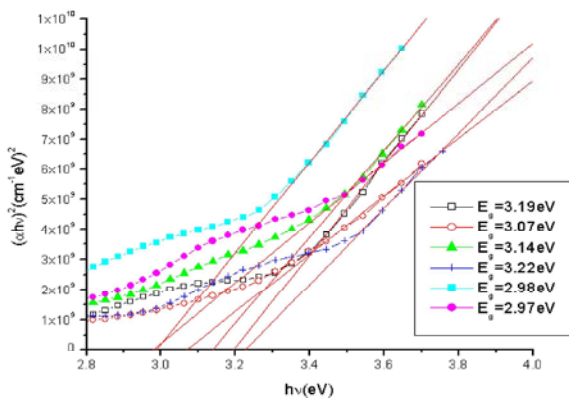


Fig. 4: Direct allowed transitions of Fe-doped SnO_2 thin films in various Fe-doping level

RESULTS AND DISCUSSION

The X-ray diffraction patterns for glass substrate, Co-doped SnO_2 thin films in various Co-doping level at 0 to 12 mol% and pure iron oxide are shown in Figure 1.

No peaks corresponding to the pure cobalt oxide film were observed, indicating that cobalt gets incorporated into the tin oxide lattice.

There is no shift in the peak positions and all the diffraction peaks can be similarly assigned to the tetragonal cassiterite SnO_2 phase and preferred orientation (110) that may be followed by (101) plane. Comparing the intensity of the series of XRD patterns, we noted that the intensities of diffraction peaks became weaker with increasing doping concentration but no impurity peak was observed. No diffraction peak related to other secondary phases was observed, indicating good purity of the final product.

The scanning electron microscopy (SEM) images of the pure SnO_2 sample and those doped with 4%, 8% and 12% cobalt are presented in Figures 2(a)-(d) respectively. It can be clearly seen from the SEM images that pure and doped SnO_2 particles are in nano-meter range between 10 nm and 100 nm and have almost spherical shape. It is observed that the particle size decreases with increase in the Co concentration in SnO_2 host matrix and size distribution of nano particles is more uniform with increasing Co dopant. These results are in good agreement with the XRD results.

The optical transmittance of Co-doped SnO_2 thin films in the visible region is shown in Figure 3. The average transmittance of the films decreased when the doping level increased from 0 mol% to 12 mol%. In general, in the visible region of the spectra, the transmission of SnO_2 thin films was very high, due to the fact that the reflectivity was low and there was less absorption due to excitation of electrons from the valence band to the conduction band [14]. In the present work, the transmission of thin films fell with increasing Co-doping concentration because the reflection and absorption increased in this range [15].

Co-doping also has influence on optical band gap of the Co-doped SnO_2 films. Data from this study showed the direct optical band gap of Co-doped SnO_2 thin films for Co-doping levels in the range 0 to 12 mol% were found to be 3.19 to 2.97 eV, respectively (Figure 4). It should be noted that reduction in optical band gap was observed after Co-doping which is consistent with the direct optical band gap of various Co-doped SnO_2 thin films.

CONCLUSIONS

This work has reported the preparation and characterization of the Co-doped tin oxide thin films in various Co-doping levels. Cobalt-doped tin oxide thin films have been successfully synthesized by spray pyrolysis method. The XRD results showed that the Co addition controlled the crystallinity of the SnO_2 powders. The direct optical band gap (E_g) of powders for Co-doping level in the range 0 to 12 mol% were decreased from 3.19 to 2.97 eV respectively. The SEM study shows the ultrafine spherical particles with a homogenous distribution.

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