



Structural and Vibrational Studies on Co²⁺ Doped SnO₂ Thin Films

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Abstract: Tin Oxide (SnO₂) thin film is one of the important transparent conducting oxides and applied in various fields such as in solar cells, optoelectronic devices, heat mirror, gas sensors, etc due to its electrical and optical transparency in visible light spectrum. Co²⁺ doped tin oxide thin films were prepared by chemical spray pyrolysis synthesis and characterized by different spectroscopic techniques. Powder XRD data revealed that the crystal structure belongs to tetragonal rutile phase and its lattice cell parameters, average crystallite size were evaluated. The morphologies of prepared sample were analyzed by using SEM and TEM studies. Vibrational bands of the prepared sample were observed in the FT-IR spectrum.

Keywords: Co-SnO₂, Thin films, Spray pyrolysis, Scanning electron microscope, Transmission electron microscope and FT-IR.

Introduction:

Metal oxide semiconductor sensor technology is based on the change in resistance of a sensitive metal oxide layer which is induced by the interaction between a surface and ambient gases [1]. Semiconductor oxide thin films are materials with numerous applications in electronic and optoelectronic devices as well as some other applications such as protective coatings, heat mirrors and catalysis [2].

Tin Oxide is an n-type semiconductor with wide energy band gap (3.7 eV). Numerous works have been reported concerning doped and undoped tin oxide thin films using various preparation techniques such as RF magnetron sputtering [3], vacuum evaporation [4], pulsed laser deposition [5], spray pyrolysis [6], sol-gel [7], chemical vapor deposition [8] and successive ionic layer adsorption and reaction [9]. Among these techniques, spray pyrolysis has proved to be simple, reproducible and inexpensive, as well as suitable for large area applications. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coatings make them useful for industrial as well as solar cell applications. In addition, spray pyrolysis opens up the possibility to control the film morphology and particle size in the nm range. As demonstrated [10], spray pyrolysis is a versatile technique for deposition of metal oxides. In the present work, Co²⁺ doped (0.01 mol %) SnO₂ thin films were prepared by using chemical spray pyrolysis method. The prepared thin films were characterized by powder XRD, SEM with EDS, TEM and FT-IR studies to collect the information about the structural properties of the prepared sample.

Experimental:

All the chemicals used in the work were of analytical grade. Mn²⁺ doped SnO₂ thin films were prepared by chemical spray pyrolysis. Spray solution was prepared by mixing 0.1 M aqueous solutions of SnO₂ and CoO (0.01 mol %) using a magnetic stirrer. The automated spray solution was then transferred to the hot substrate kept at the normalized deposition temperature of 673 K using filtered air as carrier gas at a flow rate normalized to approximately (1.8) ml/min. To prevent the substrate from excessively cooling, the prepared solution was sprayed on the substrate for 10 s with 15 s intervals. The films deposited onto micro-glass slides were first cleaned with detergent water and then dipped in acetone. Powder X-ray diffraction patterns of the prepared samples are recorded on PANalytical Xpert Pro diffractometer with CuK α radiation. Scanning electron microscope (SEM) and energy dispersive spectrum (EDS) images are taken on ZEISS EVO 18. Transmission electron microscope (TEM) images are recorded on HITACHI H-7600 and CCD CAMERA system AMTV-600 by dispersing samples in ethanol. Bruker FT-IR spectrophotometer is used for recording FT-IR spectrum of the prepared samples in the region 400-4000 cm⁻¹.

Results and discussion:

Co²⁺ doped tin oxide thin films were prepared by chemical spray pyrolysis synthesis and subsequently characterized by Powder XRD, SEM, TEM and FTIR studies.

Powder X-ray diffraction studies:

The XRD pattern of Co²⁺ doped SnO₂ optimized samples is in good agreement with the reference pattern of tin oxide with standard diffraction data of JCPDS file No. 41-1445. The diffraction data is indexed to tetragonal rutile phase of tin oxide which belongs to the space group P4₂/mnm and the corresponding lattice cell parameters are evaluated as a = b = 0.479 nm and c = 0.323 nm. The analysis of X-ray diffraction pattern revealed that the prepared tin oxide films are pure crystalline in nature. It is observable from the XRD pattern of Co²⁺ doped tin oxide films grow along the preferred orientation of (110). The average crystallite size of the prepared sample is calculated by using Debye-Scherrer's formula,

$$D = (k\lambda/\beta\cos\theta)$$

where k is a constant (about 0.9), λ is wavelength of X-ray radiation (1.5405 Å), β is full width at half maximum (FWHM) intensity of the diffraction line and θ is diffraction angle. Based on the value of FWHM, the average crystallite size is estimated to be 25 nm, which is in the order of nano-size.

Morphological studies:

The morphology and chemical composition of as synthesized thin film was investigated by SEM and EDS analysis. Fig. 1 shows the SEM micrographs of Co²⁺ doped SnO₂ thin films taken with different magnifications. SEM images reveal that the sample consists of irregular shaped sphere like structures. The incorporation of cobalt into the host material was confirmed by EDS measurements. The observed EDS pattern was shown in Fig. 2. The pattern showed the elemental compositions of Sn, O and Co. From this it was confirmed that the arranged samples contains doped cobalt species. TEM measurements were performed to confirm the nano-crystalline environment of the samples and to study the morphology of the particles. The TEM images of Co²⁺ doped SnO₂ thin films are depicted in Fig. 3.

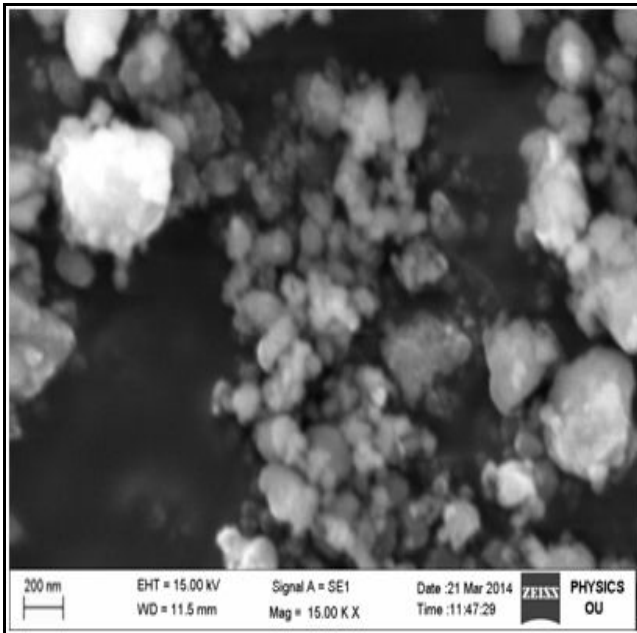


Fig. 1 SEM image of Co²⁺ doped SnO₂ thin films

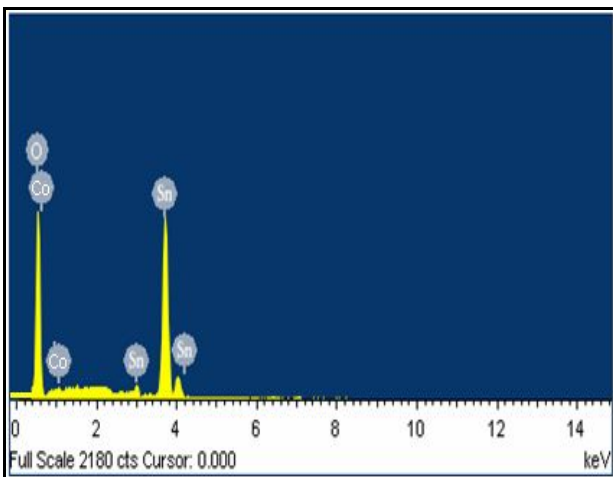


Fig. 2 EDS spectrum of Co²⁺ doped SnO₂ thin films

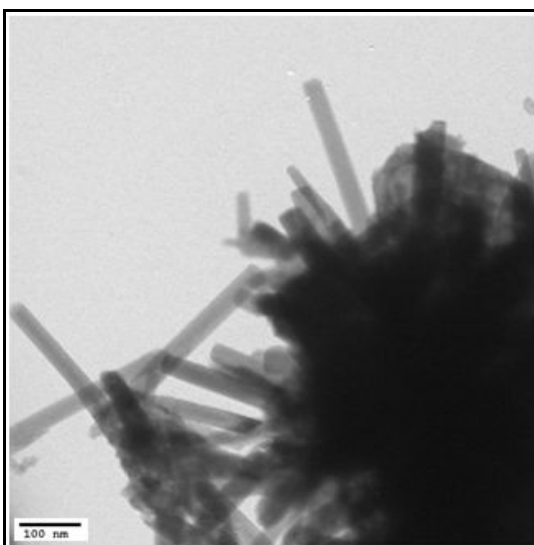


Fig. 3 TEM image of Co²⁺ doped SnO₂ thin films

FT-IR Studies:

FT-IR spectrometry was used for the determination of existing vibrational bands of the prepared sample. The bands at the low wave numbers ($500-1000\text{ cm}^{-1}$) could be attributed to SnO_2 . The peaks at 672 , 788 and 969 cm^{-1} were assigned to O–Sn–O, Sn–O–Sn stretching vibrations and lattice vibrations, while the peaks at 566 and 863 cm^{-1} were due to Sn–OH bonds of the SnO_2 crystalline phase [11]. The bands observed in the region $2500-1640\text{ cm}^{-1}$ are due to symmetric and asymmetric vibrations of hydroxyl ions situated at different sites in the lattice.

Conclusions:

Co^{2+} doped SnO_2 thin films were prepared effectively by chemical spray pyrolysis method. From the powder X-ray diffraction study, the crystal system is indexed to tetragonal rutile phase and the lattice cell parameters are evaluated. The evaluated average crystallite size of Co^{2+} doped SnO_2 thin films is in the order of nano size. SEM micrographs shows irregular shaped sphere like structures and EDS analysis confirms the presence of ingredient essentials of the prepared material. TEM images clearly show the formation of nano rods. FT-IR spectrum showed the characteristic vibrational modes of host lattice.

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