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Spectroscopic Studies on VO²⁺ Doped SnO₂ Thin Films by Spray Pyrolysis.

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ABSTRACT

Two dimensional semiconductors have been widely studied because of their novel properties and wide range of applications. Because of its high electrical conductivity, high optical transparency in the visible part of the electromagnetic spectrum, tin oxide (SnO₂) has become a promising material. Chemical spray pyrolysis method was employed to deposit VO²⁺ doped SnO₂ thin films successfully. X-ray diffraction studies revealed the crystal system is indexed to be tetragonal rutile phase. The average crystallite size of VO²⁺ doped SnO₂ thin film is found to be 22 nm. SEM studies showed irregular shaped particle size clusters. EDS analysis confirms the presence of constituent elements in the material. FT-IR spectrum showed the characteristic vibrational modes of constituent elements in the host lattice.

Keywords: SnO₂, Spray pyrolysis, VO²⁺ ions, XRD, SEM and FTIR.

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INTRODUCTION

There has been considerable interest in use of thin films in solar cell devices nowadays. Tin oxide is a semiconductor material. The electrical properties of tin oxide thin films can be suitably controlled by altering the deposition conditions. Tin oxide materials draw great attention in the fields of catalysis, photograph, electronics, photonics, data storage, optoelectronics, biological labeling, imaging and bio-sensing. Semiconductor sensor technology is based on the change in resistance of a sensitive metal oxide layer induced by the interaction between a surface and ambient gases [1]. These thin films have different applications in electronic and optoelectronic devices as well as in protective coatings, heat mirrors and catalysis [2]. This is because tin dioxide based thin films with large bandgap n-type semiconductors are attractive from the scientific and technological point of view [3].

SnO₂ thin films in the form of nanoparticles, overlayers, clusters etc. are known to exhibit enhanced sensitivity, better selectivity and fast response speeds to various reducing gases [4]. SnO₂ sensor is invariably anion deficient. The oxygen vacancies are mainly responsible for making available free electrons for the conduction process [5]. The development goes with the explosion of scientific and technological breakthrough in microelectronics, optoelectronics and nanotechnology. Tin dioxide is n-type wide bandgap semiconductor ($E_g = 3.6$ eV). SnO₂ films have several potential applications such as in transparent electrodes, film resistors, electric conversion films, heat reflective mirror, far-infrared detectors and high efficiency solar cells. Thin films of SnO₂ are synthesized by RF magnetron sputtering, metal organic chemical vapor deposition, vacuum evaporation, pulsed laser deposition, pulsed electron beam deposition, spray pyrolysis, sol-gel, chemical vapor deposition and successive ionic layer adsorption and reaction.

Tin oxide thin films are deposited by different technique. These include spray pyrolysis, chemical vapor deposition, ion-beam assisted deposition, sputtering and sol-gel methods [6-10]. Spray pyrolysis has proved to be simple, reproducible and inexpensive. Besides the simple experimental arrangement, high growth rate and mass production capability for large area coatings make them useful for solar cell application. Spray pyrolysis controls the film morphology and particle size. As demonstrated, It is a versatile technique for deposition of metal oxide thin films. Rao et al. have presented the results on different oxide materials in their earlier studies [11-20]. In the present investigation, VO²⁺ doped (0.01 mol %) SnO₂ thin films were prepared by using chemical spray pyrolysis method and characterized by XRD, SEM with EDS, TEM and FT-IR studies.

EXPERIMENTAL

The chemicals used in the present work were of analytical grade. VO²⁺ doped SnO₂ thin films were prepared by chemical spray pyrolysis. Spray solution was prepared by mixing 0.1 M aqueous solutions of SnO₂ and V₂O₅ (0.01 mol %) using 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. The prepared solution was sprayed on the substrate for 10 s with 15 s intervals in order to prevent the substrate from excessively cooling; the films deposited onto micro-glass slides were first cleaned with detergent water and then dipped in acetone.

X-ray diffraction patterns were 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

VO²⁺ doped tin oxide thin films were prepared by chemical spray pyrolysis synthesis and subsequently characterized by XRD, SEM, TEM and FTIR studies.

Powder X-ray diffraction Studies

Figure-1 shows the X-ray diffraction pattern of VO²⁺ doped SnO₂ thin films. The XRD pattern of these 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 be tetragonal rutile phase of tin oxide which belongs to the space group $P4_2/mnm$. The corresponding lattice cell parameters are evaluated as $a = b = 0.467$ nm and $c = 0.321$ nm respectively. X-ray diffraction pattern revealed that the prepared tin oxide films are pure crystalline in nature. It is perceptible from the XRD pattern of VO^{2+} 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

D is the mean crystallite size,

K = 0.9 is Scherrer's constant,

λ is the wavelength of the incident beam,

θ is the diffraction angle,

and β is the full width half maximum intensity of the diffraction peak.

From the XRD pattern, the calculated value of average crystallite size is 22 nm.

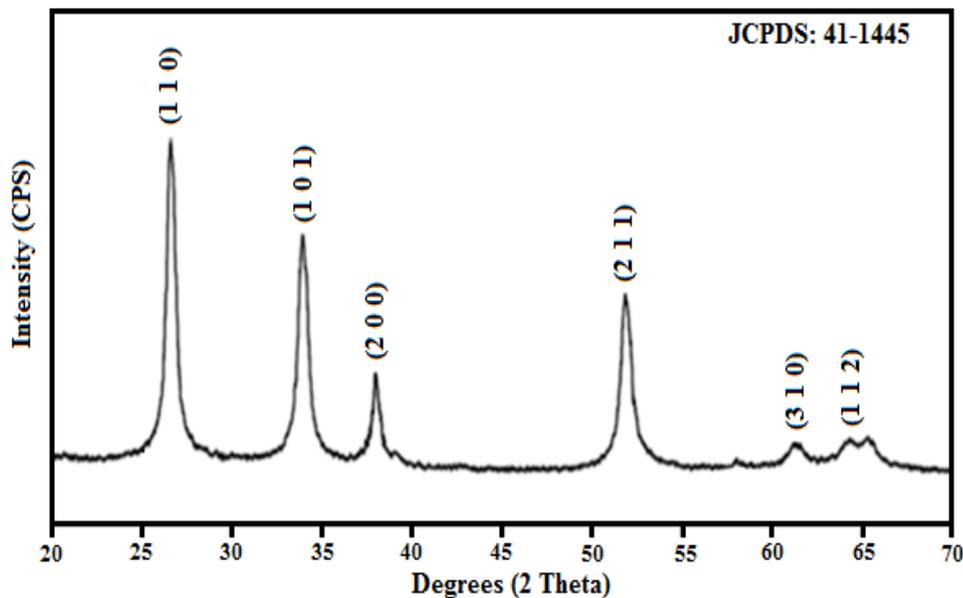


Figure-1: Powder X-ray diffraction pattern of VO^{2+} doped SnO_2 thin films

Morphological Studies

SEM and EDS analysis was used to study the morphology and chemical composition of as synthesized sample. Figure-2 shows the SEM micrographs of VO^{2+} doped SnO_2 thin films taken with different magnifications. It can be clearly observed from low resolution SEM images that the prepared sample shows agglomeration with an irregular morphology. The agglomeration could be induced by densification resulting from the narrow space between particles. SEM reveals the sample consists of irregular shaped sphere like structures. The incorporation of vanadium into the host material was confirmed by EDS measurements. The observed EDS pattern was shown in Figure-3. The pattern showed the elemental compositions of Sn, O and vanadium. From this it was confirmed that the prepared samples contain doped vanadium species. TEM measurements were performed to confirm the nanocrystalline nature of the samples. TEM images of VO^{2+} doped SnO_2 thin films are depicted in Figure-4. The particles are more or less uniform in size and of irregular shape.

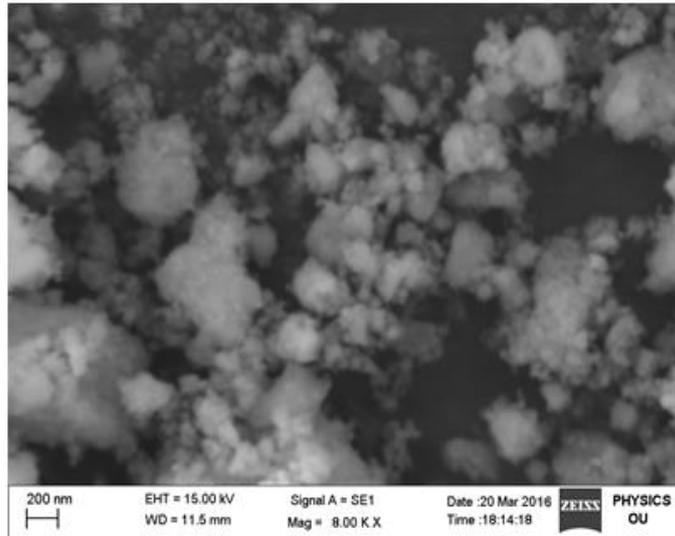


Figure-2: SEM image of VO²⁺ doped SnO₂ thin films

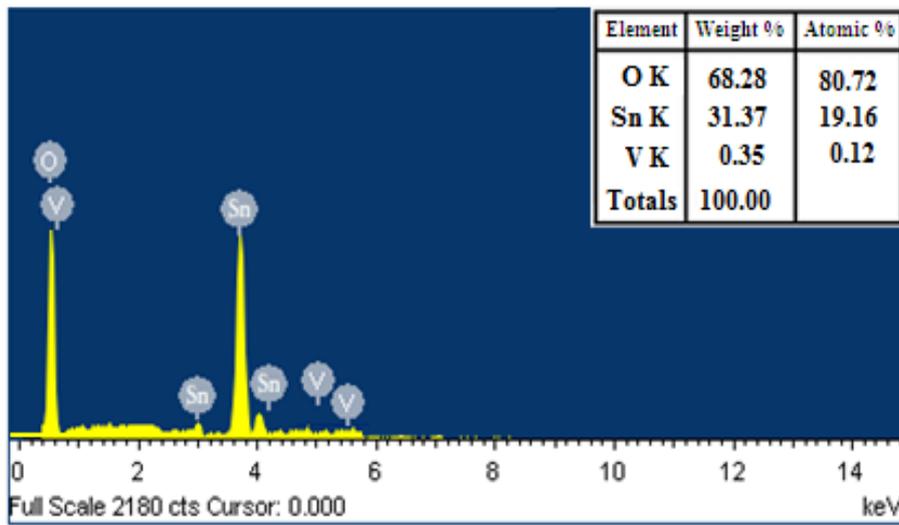


Figure-3: EDS spectrum of VO²⁺ doped SnO₂ thin films

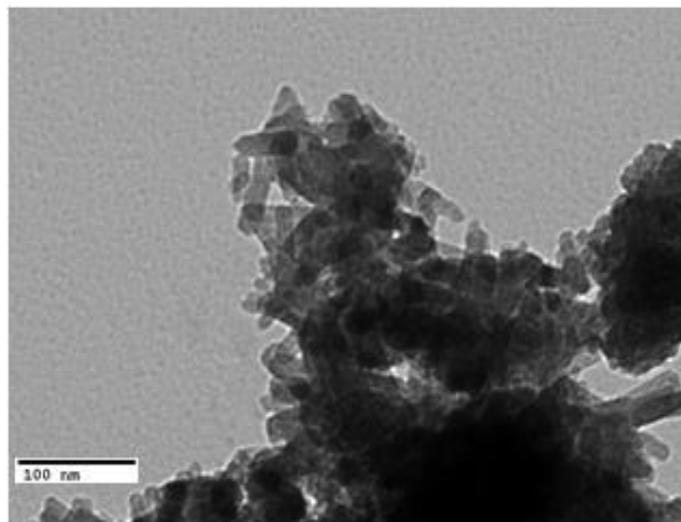


Figure-4: TEM image of VO²⁺ doped SnO₂ thin films

FT-IR Studies

FT-IR spectrometry was used for the determination of existing surface species. The FT-IR spectrum of VO²⁺ doped SnO₂ thin films was illustrated in Figure-5. The bands at the low wavenumbers (500-1000 cm⁻¹) could be attributed to SnO₂. The peaks at 678, 785 and 961 cm⁻¹ were assigned to O–Sn–O, Sn–O–Sn stretching vibrations and lattice vibrations, while the peaks at 565 and 869 cm⁻¹ were due to Sn–OH bonds of the SnO₂ crystalline phase [21]. The bands observed in the region 2500-1640 cm⁻¹ are due to symmetric and asymmetric vibrations of hydroxyl ions situated at different sites in the lattice.

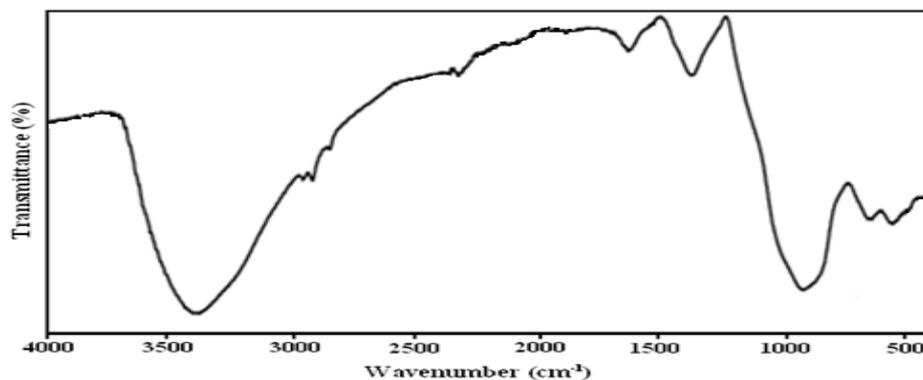


Figure-5: FT-IR spectrum of VO²⁺ doped SnO₂ thin films

CONCLUSIONS

VO²⁺ doped SnO₂ thin films were prepared successfully by chemical spray pyrolysis method. X-ray diffraction studies revealed the crystal system is indexed to be tetragonal rutile phase. The calculated average crystallite size of VO²⁺ doped SnO₂ thin films is 22 nm. SEM micrographs show irregular shaped sphere like structures. EDS analysis confirms the presence of constituent elements in the prepared material. TEM images clearly show the formation of nanorods. FT-IR spectrum showed the characteristic vibrational modes of host lattice.

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