Structural and optical analysis of SnO₂ thin films BY Spray Pyrolysis

S. Roguai¹, A. Djelloul

¹LASPI²A Laboratoire des Structures, Propriétés et Interactions Inter Atomiques, Université Abbes Laghour, Khencela 40000, Algérie.

*Corresponding author: rog.sabrina@yahoo.fr ; Tel.: +213 00 00 00 ; Fax: +21300 00 00

I. Introduction

Oxides (TCO) are interesting materials because of their unique characteristics such as high electrical conductivity and high transparency which makes ideal candidates for many applications such as optoelectronics, photovoltaic and catalytic applications [1] Zinc Oxide (ZnO) & Tin Dioxide (SnO₂) are among the TCOs which offer most accurately an exceptional choice for the electronic devices synthesis on the hand [2-4]. And they are used to obtain thin films for the purpose of manufacturing solar cells, on the other hand [1]. SnO₂ is n-type semiconductor with high conductivity due to the presence of structural defects (VO) in its rutile tetragonal structure in addition to their transparency with a gap energy of 3.6 eV at 300K [5-7] Several techniques have been used to develop tin oxide thin layers of such as sol-gel [8], pulsed laser deposition [9], RF sputtering [10] and spray pyrolysis [11-16]. The ultrasonic pyrolysis spray has many advantages, such as their simplicity to prepare thin films with large surface area from high purity materials. The obtained films have a great homogeneity, a well controlled stoichiometry, can be treated at low temperature. The best advantage is its low cost [17].

In this work, we studied the structural and optical properties, of SnO₂ thin films deposited by the ultrasonic pyrolysis spray technique (USP). Theoretical relationships are used to obtain the dispersion parameters of the films from a single experimental transmission spectrum.

II. Experimental Part

II.1. Film preparation

SnO2 thin films were prepared by USP method. The utilized solution for the elaborated films has the following composition: 0.01 M of tin chloride [SnCl₄, 2H₂O] (Fulka 99.9 %) is used as the Sn source; 50 ml deionized water (resistivity=18.2 MΩ·cm); 20 ml CH₃OH (Merck 99.5 %); 30 ml C₂H₅OH (Merck 99.5 %). Details are listed in the works [17]

II.2. Characterization techniques

The thin films were characterized by XRD, SEM, FTIR and optical absorption and photoluminescence properties are thoroughly studied. Structural properties recorded using diffractometer high resolution Rigaku Ultima IV powder equipped with Cu-Kα radiation (λ= 1.5418 Å). The surface morphologies of nanoparticles were
characterized by using scanning electron microscopy (SEM) (FEI Quanta TM 250 FEG). The optical properties were estimated utilizing a Perkin Elmer UV-VIS-NIR Lambda 19 spectrophotometer in the 190-1800 nm spectral range. The FTIR spectra were recorded using Thermo-Nicolet equipment in the 4000-400 cm⁻¹ region. Photoluminescence measurements of prepared samples were examined using Perkin-Elmer LS 45 Fluorescence spectrometer with excitation wavelength of 350 nm.

III. Results and discussion

III.1. Structure analysis

X-ray diffraction patterns of as-prepared pure SnO₂ in Figure 1 reveal the formation of tetragonal Rutile structure as confirmed with (JCPDS Card No. 00-041-1445) with space group P42/mnm. located at 20 values 27.2°, 34.4°, 38.4°, 52.2°, 55.1° and 62.1° and their Miller indices were (110), (101), (200), (211), (220) and (310) respectively [18,19]. A preferred orientation along (110) direction [20] is observed, no apparent reflection (impurities) were observed which indicated the synthesized samples were purely single phase [21].

![Figure 1. XRD patterns of SnO₂.](image)

### Table 1. Structural parameters of SnO₂ nanoparticles

<table>
<thead>
<tr>
<th>2θ value (°)</th>
<th>FWHM (°)</th>
<th>d-Value (Å)</th>
<th>a =b (Å)</th>
<th>c (Å)</th>
<th>c/a</th>
<th>V (Å³)</th>
<th>Average crystal size (D) (nm)</th>
<th>Micro-strain (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>27.2422</td>
<td>0.2466</td>
<td>3.3470</td>
<td>4.7333</td>
<td>3.1854</td>
<td>0.6729</td>
<td>71.3661</td>
<td>33</td>
</tr>
</tbody>
</table>

III.2. Morphological studies of SnO₂ nanoparticles

Figure 2 shows nano-particles of SEM images of SnO₂. The surface morphology is uniform and appears as a distribution of small granular shaped particles evenly distributed throughout it [25]. Crystalline size: 100 nm.
Figure 2. SEM images of SnO$_2$ thin films

III.3. FTIR Analysis

FT-IR spectroscopy is used to identify the adsorbed functional group from their frequencies. Figures 3, 4 shows the FTIR spectra for SnO$_2$ film recorded between 400cm$^{-1}$ and 4000cm$^{-1}$ at room temperature. Two large peaks around 3444cm$^{-1}$ and 1624cm$^{-1}$ are observed due to the vibrations of the hydrogen bond involved in the O-H oscillators in the adsorbed water molecules and in the alcohol respectively [26] and small peaks around 1023cm$^{-1}$, 1384 cm$^{-1}$and 2356 cm$^{-1}$denote the hydrogen bonds involved in O-H oscillators and peaks around 2849 cm$^{-1}$ and 2356 cm$^{-1}$may be due to the CO$_2$ absorption from the ambient air atmosphere [27-29]. And two bands appearing around 574 cm$^{-1}$ and 665 cm$^{-1}$for are due to the Sn-O-Sn vibration and the Sn-O bond in SnO$_2$ which confirms the existence of SnO$_2$ [26, 30-32].

Figure 3. FTIR spectra of SnO$_2$ films grown onto glass substrate by ultrasonic spray pyrolysis at 450°C in the range 400-4000 cm$^{-1}$

Figure 4. FTIR spectra of SnO$_2$ films grown onto glass substrate by ultrasonic spray pyrolysis at 450°C in the interval 520-680 cm$^{-1}$.

III.4. Optical properties

Figure 5 shows the transmission spectrum of SnO$_2$ deposited on a glass substrate. The spectrum obtained as a function of the wavelength (190-1100 nm). The solid curve corresponds to the curve fitting and the symbol represents the experimental data. The Figures reveal a reasonably good fitting to the experimental data [33]. Although the general pattern of the spectra is that they are composed of two regions:

- A region of strong absorption. This region corresponds to the fundamental absorption ($\lambda <400 \text{ nm}$) in the films. This absorption is due to the interband electronic transition. The variation of the transmission in this region is exploited for the determination of the gap.
- A region of high transparency located between 400 and 1100nm, the values of the transmission is of the order of 68.9%. This value gives our thin layers obtained by pyrolysis Spray, the transparency character in the visible.

The value obtained from the Eg as well as the thickness and $n$ at 598 nm, extracted by fitting [33] the experimental data are listed in Table 2. The value of the bandgap obtained is in accordance with the known value of SnO$_2$ [34, 35].
Table 2. Dispersion parameters of the films extracted by fitting the experimental data [33].

<table>
<thead>
<tr>
<th></th>
<th>Thickness (nm)</th>
<th>( E_g ) (eV)</th>
<th>( n ) at 598 (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO(_2)</td>
<td>583</td>
<td>3.838</td>
<td>1.697</td>
</tr>
</tbody>
</table>

Figure 5. Transmission spectrum of SnO\(_2\) films deposited on glass substrate at 450 °C. Measured (full circles) and calculated (solid lines) transmittance spectra of films.

Figure 6. Refractive index of SnO\(_2\) films grown on glass substrate at \( T_s = 450 \) °C.

III.5. Photoluminescence properties

In Figure 7, PL spectra consist of four emission peaks centered about 407, 419, 484 and 529 nm. As energy corresponding to all the observed emission peaks (3.04, 2.95, 2.56 and 2.34 eV) is lower than the band gap energy of the film [17,34]. The first two bands P1 and P2 located in the violet emission show the donor-acceptor recombination (DAP) due to the electronic transition between the two valence and conduction band is exactly donor close to the (BC) and acceptor levels near the top of the (BV) [17,35]. The two emissions P3 and P4 may be due to the electronic transition from the deep donor level formed by the oxygen vacancies to the valence band in the film [17,36].

Figure 7. PL spectra of SnO\(_2\) thin films measured at room temperature.

IV. Conclusion

SnO\(_2\): Thin layers were deposited by the Pyrolysis Spray technique on glass substrates at 450 °C at 30 min. The obtained films are polycrystalline with the tetragonal structure and have a (110) preferred orientation, found uniform surface morphology with small granular shaped particles distributed throughout the surface. The FTIR study indicated the existence of two distinct characteristic absorption peaks at 574 cm\(^{-1}\) and 665 cm\(^{-1}\) for the mode of vibration of deformations (O-Sn-O) and of stretching (O-Sn) respectively. From the transmittance spectra, we have deduced the optical gap \( E_g \) as well as the thickness and the refractive index of SnO\(_2\) films by the model of Wemple and DiDomenico. Photoluminescence spectroscopy reveals the presence of intrinsic defects.

Acknowledgments

The authors would like to thank the National Project Research (PNR) and LASPI2 Laboratory of Khenchela University (Algeria) for their financial support of this research project.

V. References


doi.org/10.1007/s00339-019-3118-3


29. Sivajahnavi, V.; Tripathy, S.K.; Ramalingeswara Rao, A V N. Structural, optical, magnetic and dielectric studies of SnO₂ nanoparticles in real time.


33. Roguai, S.; Djelloul, A.; Nouveau, C.; Souier, T.; Dakhel, AA.; Bououdina, M. Structure, microstructure and determination of optical constants from transmittance data of co-doped Zn$_{0.90}$Co$_{0.05}$M$_{0.05}$O (M = Al, Cu, Cd, Na) films. *Journal of Alloys Compounds* 599 (2014) 150-158.


Please cite this Article as: Roguai S., Djelloul A., Structural and optical analysis of SnO$_2$ thin films by spray pyrolysis, *Algerian J. Env. Sc. Technology*, X:X (YYYY) XX-XX