Concentration influence on structural and optical properties of SnO₂ thin films synthesized by the spin coating technique.

Soumia Belhamri, Nasr-Eddine Hamdadou
Laboratoire de Micro et de Nanophysique (LaMiN), Ecole Nationale Polytechnique d'Oran (ENPOran), BP 1523 El Mnaouer, Oran 31000, ALGERIE
Email: somimira@live.fr

Abstract. Tin dioxide is an n-type semiconductor, with wide band gap 3.6 eV and special properties such as high optical transmission in the visible range, the infrared reflection and chemical stability. The objective of our work is to study the effect of solution concentration on the properties of SnO₂ thin films, which were deposited on glass substrate by sol-gel spin coating technique and characterized by X-ray diffraction, UV–visible spectroscopy after annealing for one hour at 500°C.

X ray diffraction spectra (XRD) showed that the films deposited at different concentrations (0.7 mol/l, 1 mol/l, 1.5 mol/l) are polycrystalline with a rutile type tetragonal. The grains have two preferred orientations along the directions (110) and (101) corresponding to \(2\theta = 26.744°\) and \(34.113°\) respectively. We have also noted that the grain size change between 20 and 40 nm. The peak of diffraction becomes less intense when the solution concentration is more than 0.7 mol / l. The optical transmission of the films in the visible spectrum was in the range of 59 - 44%.

Keywords: Thin film, SnO₂, spin coating, structural and optical properties.

1. Introduction

Environmental protection has become the objective of many the current researches and the most important of these inventions use the technology photovoltaic. The best known are probably the modules based on polycrystalline silicon, which still occupy the greater part of the PV market. Less known are the thin-film modules, which are often described as second-generation photovoltaic modules. These thin-film solar modules offer several advantages like the absence of raw materials and use the low-cost materials such as tin dioxide, which is the subject of our study. The tin dioxide is one of the most used oxides in the photovoltaic cells [1] because of its specific properties such as an n-type semiconductor with a large gap (3.6-4.0 eV) [2,3], a high optical transmission in the visible range [4], with a rutile structure (tetragonal), the lattice parameters \(a = b = 4.737\) Å and \(c = 3.816\) Å, [5]. The grain size is typically between 200-400 Å which are highly dependent on the deposition technique, temperature, doping level etc. [6-7].

2. Experimental

2.1. Preparation of thin films:

In our work we used the spin coating technique or centrifugation. This method is simple to implement, low energy costs and lead to very pure and homogeneous materials with a thin thickness.
SnO₂ thin films are grown on glass substrates rectangular (25 x 10 x 1) mm³ cut by a rod made of alumina. The cleaning of the substrates is very important to obtain films with good adhesion to the substrate and good structural and morphological properties. The substrates were first cleaned with acetone for 15 minutes at room temperature, and then dipped in distilled water for 10 minutes. Afterwards, the substrates were cleaned with Betadine (medical soap) to remove the last traces. Finally, they were rinsed in distilled water.

The solution was prepared by dissolving the precursor of tin chloride (SnCl₂·2H₂O) in ethanol (C₂H₅OH) as solvent at room temperature; the solution was stirred at 80°C for 1h until obtaining a yellow color. Then put it in a flask under room temperature for 24h. After cleaning the substrate, we are putting in the spin coater for depositing a small puddle of solution onto the center of them and then spinning the substrate at high speed. Centripetal acceleration will cause the solution to spread off the edge of the substrate. The following step is the drying: When we evaporating the volatile liquids on the heating plate, we get a thin film. We have repeated these steps 10 times to obtain a considerable thickness.

| Table 1. Deposition parameters for SnO₂ thin film. |
|-----------------------------------------------|
| Substrate temperature | 120°C for 10 min |
| Concentration of solution | 0.7 - 1 - 1.5 mol l⁻¹ |
| Rotation speed | 3000 rpm |
| Number of cycles | 10 |
| Deposit time | 30 s |
| Solutions | tin chloride [SnCl₂] in ethanol |
| Acceleration | 600 rpm / min. |
| PH | 2 |

After the deposition, thin films of SnO₂ are annealed in an oven for 1 hour at 500°C. This step improves the crystallization of the film and the thermally stabilize.

2.2. Characterization of SnO₂ thin films:
Structural analysis of the films were carried out by BRUKER diffractometer using Cu Kα₁ radiation (λ=1, 54056 Å). Diffractograms were recorded from 10° to 80° with a step of 0.01°. The optical absorption and transmittance were studied with UV–vis spectrophotometer, 210 SPECORD Plus® in the wavelength range of 100–1200 nm at room temperature.

3. Results and discussion

3.1. X-ray diffraction studies:
Figs. (1), (2) and (3) presents the XRD patterns of the SnO₂ thin films prepared with different concentration. As can be observed, the SnO₂ thin film appears to have a polycrystalline structure with a cassiterite tetragonal crystalline phase according to reference pattern of JCPDS (41-1445). The value of lattice parameters were found to be a = b = 4.69 Å and c =3.16 Å, which are in good agreement with the reported bulk values (a = 4.7382 Å, c = 3.1871 Å). [8]. SnO₂ film showed a random orientation along (110) and (101) planes.

The average grain size was calculated using Scherrer formula:
Where $D$ is the mean grain size of the nanoparticles, $K = 0.9$ and $\lambda = 1.5406 \text{ Å}$ and $\beta$ is the full width half maximum (FWHM) of the diffraction peaks.

Crystallite sizes of the samples were found between 17 and 39.8 nm, see Tables (2), (3) and (4). The grain size is small which leads to a very intense grain boundary scattering, and then a low mobility, that means the films are resistive. This small grain size causes high surface energy.

It is manifested that as the concentration solution decreases, the intensity of the peaks particular (110) plane gets enhanced, which shows that the films deposited at low concentration have better crystallinity.

Figure 1. XRD patterns of SnO$_2$ thin films with a concentration 0.7 mol / l after annealing at 500°C.

Figure 2. XRD patterns of SnO$_2$ thin films with a concentration 1 mol / l after annealing at 500°C.

Figure 3. XRD patterns of SnO$_2$ thin films with a concentration 1.5 mol / l after annealing at 500°C.
Table 2. The crystalline parameter values of SnO$_2$ thin film with a concentration of 0.7 mol/l after annealing at 500°C.

| $2\theta$ (deg) | hkl   | D (nm) | I (u.a) | $I_0$ (%) | $d_{hkl}$ (Å) | FWHM (deg) |
|----------------|-------|--------|---------|-----------|---------------|------------|
| 26.744         | (110) | 36.808 | 645     | 100       | 3.335         | 0.387      |
| 34.113         | (101) | 31.177 | 833     | 75        | 2.6262        | 0.465      |
| 38.117         | (111) | 31.535 | 580     | 21        | 2.359         | 0.465      |
| 51.987         | (211) | 16.598 | 198     | 57        | 1.757         | 0.929      |
| 54.714         | (220) | 20.136 | 446     | 14        | 1.6763        | 0.775      |
| 64.917         | (112) | 28.970 | 78      | 12        | 1.435         | 0.567      |

Table 3. The crystalline parameter values of SnO$_2$ thin film with a concentration of 1 mol/l after annealing at 500°C.

| $2\theta$ (deg) | hkl   | D (nm) | I (u.a) | $I_0$ (%) | $d_{hkl}$ (Å) | FWHM (deg) |
|----------------|-------|--------|---------|-----------|---------------|------------|
| 26.796         | (110) | 20.441 | 372     | 100       | 3.324         | 0.697      |
| 34.066         | (101) | 26.745 | 396     | 75        | 2.629         | 0.542      |
| 38.326         | (111) | 31.554 | 207     | 21        | 2.346         | 0.465      |
| 42.122         | (210) | 24.044 | 284     | 1         | 2.143         | 1.859      |
| 52.200         | (211) | 39.880 | 161     | 57        | 1.750         | 0.387      |

Table 4. The crystalline parameter values of SnO$_2$ thin film with a concentration of 1.5 mol/l after annealing at 500°C.

| $2\theta$ (deg) | hkl   | D (nm) | I (u.a) | $I_0$ (%) | $d_{hkl}$ (Å) | FWHM (deg) |
|----------------|-------|--------|---------|-----------|---------------|------------|
| 26.872         | (110) | 30.59  | 278     | 100       | 3.315         | 0.465      |
| 34.090         | (101) | 23.38  | 279     | 75        | 2.627         | 0.620      |
| 42.036         | (210) | 31.930 | 98      | 1         | 2.147         | 0.465      |
| 52.302         | (211) | 33.1   | 124     | 57        | 1.747         | 0.465      |
| 55.051         | (220) | 25.208 | 72      | 14        | 1.666         | 0.620      |
3.2. UV–vis characterization:

The UV–vis spectra of films SnO$_2$ deposited at different concentration are given in Figs. (4) and (5). The absorption spectra UV-visible of SnO$_2$ thin film developed at different concentration (0.7-1-1.5 mol / l) after annealing at 500°C for 1 hour (Fig.4) showed that there is absorption over the range (300-350nm) due to the formation of SnO$_2$ crystallites. That means this concentration cause the formation of tin dioxide crystals.

![Figure 4](image)

**Figure 4.** UV-visible absorption spectra of the SnO$_2$ thin film prepared with different concentrations.

The optical transmission spectra of thin films of SnO$_2$ annealing at 500°C for 1 hour are shown in the Fig (5). The transmittance in the visible region was found to be in the range 59 - 44%. In general, in this region of the spectrum (400 and 800 nm), the transmission is high which is due to the fact that there is no absorption and the reflectivity is low.

The onset absorption edge at around 350 nm was observed in the transmission spectra of the SnO$_2$ thin films. The decrease of transmission SnO$_2$ with increasing concentration of solution can be attributed to the increase in surface roughness of the SnO$_2$.

![Figure 5](image)

**Figure 5.** Transmittance spectra of the SnO$_2$ film prepared with different concentrations.
4. Conclusion

In summary, we present our work on tin dioxide thin films prepared by spin coating technique, regarding its structural and optical properties.

The X-ray diffraction helped to identify the tetragonal structure (rutile) of SnO$_2$ with the maximum intensity peaks from (110) and (101) planes. However, the relative intensity of the peaks decreases with an increase in the concentration of solution.

Optical transmission spectra show high transparency between 400 and 800 nm with a value from 59 to 44% in the visible.

The experimental results suggest that the concentration used has an effect on the structural and optical properties.

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