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Characteristics of SnO2:F Thin Films Deposited by Ultrasonic Spray Pyrolysis: Effect of Water Content in Solution and Substrate Temperature

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ABSTRACT

Fluorine doped tin oxide, SnO2:F, thin films were deposited by ultrasonic chemical spray starting from tin chloride and hydrofluoric acid. The physical characteristics of the films as a function of both water content in the starting solution and substrate temperature were studied. The film structure was polycrystalline in all cases, showing that the intensity of the (200) peak increased with the water content in the starting solution. The electrical resistivity decreased with the water content, reaching a minimum value, in the order of $8 \times 10^{-4} \Omega \cdot \text{cm}$, for films deposited at 450˚C from a starting solution with a water content of 10 ml per 100 ml of solution; further increase in water content increased the corresponding resistivity. Optical transmittances of SnO2:F films were high, in the order of 75%, and the band gap values oscillated around 3.9 eV. SEM analysis showed uniform surface morphologies with different geometries depending on the deposition conditions. Composition analysis showed a stoichiometric compound with a [Sn/O] ratio around 1:2 in all samples. The presence of F into the SnO2 lattice was detected, within 2 at % respect to Sn.

Keywords: Tin Oxide; Ultrasonic Spray Pyrolysis; Transparent Conducting Oxides; TCO

1. Introduction

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 [1-3]. In the context of world energy demand, particularly energy conversion, transparent conductive oxides (TCOs) based on semiconductor oxides, play a crucial role in the development of new-fashioned thin film solar cells [4]. As a matter of fact, in the organic solar cells, such as in dye-sensitized nanocrystalline TiO2 solar cells (DSSCs), TCOs are used in tandem structures developed on ordinary glass and flexible substrates [5].

In this respect, TCOs for DSSCs manufacturing should present a good chemical stability due to the possible chemical reactions occurring in the manufacturing process, as in the annealing steps, and also the chemical interactions promoted by electrolytes in the line of duty, that define the lifetime of the device. In our developed work on organic thin film solar cells, we have noticed that tin oxide electrodes offer the chemical stability required for device processing, contrary to results obtained from indium oxide films that, despite the higher electrical conductivity, is presented a degradation to metallic indium during the process, which in turn affects adversely the performance of the device. The manufacturing of thin film devices based on non-sophisticated techniques, with a competitive performance has encouraged many researchers in the challenge of reaching higher efficiencies through the improvement of the material properties. Chemical deposition techniques provide a simple and economical way of processing good quality films demanded in the manufacturing of different devices. Some of the relevant chemical techniques for the deposition of quality films are sol-gel [6], homogeneous precipitation [7], chemical vapor deposition [8], and chemical spray techniques [9], among others. Results about deposition of quality SnO2 films by chemical spray technique either in pneumatic or ultrasonic atomization process have been continuously reported [10,11]. In the pneumatic process, the deposition is developed at atmospheric pressure and the system is very simple; whereas in the
ultrasonic, it is necessary a closed reaction chamber, as a
diluted fog instead of a jet of droplets is now directed on
the hot substrate. In this deposition technique any slight
disturbance generated by the exhaust system can modify
the fog pattern, causing a non uniform growth, and hence,
films with a like-rainbow finish are obtained. Neverthe-
less, according to our experience an advantage of the
ultrasonic route is the significantly saving of reactants
during the processing films.

As a consequence of the economic adaptation of the
atomization equipment, the number of reports on SnO2
thin films by ultrasonic spray is increasing now, and a
better understanding of the process involved is being
reached. Studies on the effect of post annealing treat-
ments [12], substrate temperature [13], microstructure [15],
and doping [16] have been published. E. Elangovan, et al. [11]
reported SnO2:F thin films with a resistivity in the order of $2 \times 10^{-4} \Omega \text{cm}$, starting from stannous chloride (SnCl2) and ammonium fluoride (NH4F).
Also, the role of solution preparation in the deposition of
tin oxide films by chemical spray technique has been
raised [17]. Tin oxide thin films deposited by ultrasonic
spray pyrolysis are usually reported starting from SnCl2 and
ethanol. In our case due to limitations of equipment,
methanol has been adopted as the main solvent, since this
can be atomized easily.

In this work, the effect of both water content in the
starting solutions and substrate temperature on the
physical characteristics of SnO2 films, deposited by ul-
trasonic spray pyrolysis, starting from tin chloride and
hydrofluoric acid, is reported.

2. Experimental

SnO2:F thin films were deposited by ultrasonic spray
pyrolysis from a 0.2 M starting solution of tin chloride
(SnCl4·5H2O), dissolved in a mix of water and methanol.
The water content was varied in five different volumes,
namely, 2.5, 5.0, 10.0, 20.0 and 30.0 ml for a total solution
volume of 100 ml. Hydrofluoric acid at a fixed
$[F]/[Sn]$ ratio of 30 at % was used as F precursor. The
selection of this ratio is based in previous experimental
work, where we found that the optimum fluoride doping
concentration oscillate between 20 and 40 at %.

SnO2:F samples were deposited on 2.5 cm $\times$ 5.0 cm
clean glass substrates at five different substrate tempera-
tures, namely, 375°C, 400°C, 425°C, and 450°C, at a fixed
deposition time of 12 min. The cleaning process was as
follows: 1) a five minutes ultrasonic bath in a tri-
chloroethylene for degreasing the substrates; followed by
2) a five minutes bath in methyl alcohol; 3) a five min-
utes ultrasonic bath in acetone [CH3COCH3]; and finally,
4) a drying process by a jet of gas nitrogen [N2].

The electrical sheet resistance of all as-deposited sam-
ple was measured by the four point probe technique by
using a Veeco equipment, with the appropriate geometric
correction, $\pi/\ln2 = 4.53$. The structure of the as-deposited
films was characterized by means of X-ray diffraction in a
Pan-Analytical Xpert Pro system, by using the $\theta - 2\theta$
technique, based on the Cu-Kα radiation ($\lambda = 1.5405$ Å).
Scanning electron micrographs were obtained from a Jeol
JSM 5400 LV microscope. Chemical composition of all
the SnO2 films was determined by energy dispersive
spectroscopy (EDS) with a detector MORAN (Quest) having a
136 eV resolution. The optical transmittance at
normal incidence was measured with a double-beam UV-
Vis Shimadzu spectrophotometer, in the UV-visible re-
region (300 - 1000 nm) without glass substrate correction.
The film thickness was estimated according to the Mani-
facier’s formula [18], and corroborated by direct meas-
urements with a KLA Tencor P15 profilometer. The values
estimated were around 600 nm.

3. Results and Discussion

3.1. Electrical Properties

Electrical resistivities for all as-grown SnO2:F films de-
posited were calculated from the mathematical product
of the respective sheet resistances and thickness values. In
Table 1 are listed the results obtained. From these, it can
be observed that an increase in the water content leads to
a decreasing in the electrical resistivity, reaching a
minimum magnitude in samples deposited at 450°C from
a starting solution with $\text{Vol}_\text{H}_2\text{O} / \text{Vol}_\text{TOTAL} = 10/100$. Further
increase in the substrate temperature increases the
electrical resistance of the films. These results show that
both substrate temperature and water content influence
the growth kinetic and consequently the physical proper-
ties of the films. This behavior is associated with the
variation of the F incorporation into the SnO2 lattice as
the solution conditions and deposition temperature are
changed.

Table 1. Electrical resistivity values of SnO2:F films de-
posited at different substrate temperatures, from starting
solutions with different $\text{Vol}_\text{H}_2\text{O} / \text{Vol}_\text{TOTAL}$
ratios.

<table>
<thead>
<tr>
<th>Deposition Temperature (°C)</th>
<th>2.5/100 $\times 10^4$ (Ω cm)</th>
<th>5/100 $\times 10^4$ (Ω cm)</th>
<th>10/100 $\times 10^4$ (Ω cm)</th>
<th>20/100 $\times 10^4$ (Ω cm)</th>
<th>30/100 $\times 10^4$ (Ω cm)</th>
</tr>
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<td>375</td>
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<td>82</td>
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<tr>
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<td>10</td>
<td>10</td>
<td>8</td>
<td>22</td>
<td>26</td>
</tr>
</tbody>
</table>
3.2. Structure

Figure 1 shows the X-ray diffraction spectra of SnO$_2$:F thin films deposited at 450°C from starting solutions with different water contents, for 2$\theta$ values from 20° to 70°. All samples were polycrystalline, and the peaks fit well with the different reflections of the SnO$_2$ cubic rutile structure, ASTM standard card JCPDS No. 41-1445 [19]. All spectra show the (200) direction as preferred growth orientation, whereas the (110) and (310) directions increase with the water content in the starting solution. These results demonstrate that, as was expected, the preferred growth orientation is sensible to the water content in the starting solutions. Absence of the Sn$_3$O$_4$ phase was also confirmed, as substrate temperatures higher than 400°C guarantee only SnO$_2$ formation. Additionally, no fluorine phases were detected despite the fact that a high [F/Zn] = 30 at% ratio in starting solution, was added. This result confirms the highly volatile character of fluorine compounds during the growth process, and consequently its low efficiency of incorporation into the SnO$_2$ lattice.

3.3. Morphology

Figures 2 and 3 show the variation in the surface morphology of SnO$_2$:F thin films deposited at 450°C as a function of the water content in the starting solution at different magnifications.

Figure 2. SEM micrographs at low magnification of SnO$_2$:F thin films deposited at 450°C, from starting solutions with different water content. (a) $\text{Vol}_\text{H}_2\text{O}/\text{Vol}_\text{TOTAL} = 2.5/100$; (b) $\text{Vol}_\text{H}_2\text{O}/\text{Vol}_\text{TOTAL} = 10/100$; (c) $\text{Vol}_\text{H}_2\text{O}/\text{Vol}_\text{TOTAL} = 20/100$; and (d) $\text{Vol}_\text{H}_2\text{O}/\text{Vol}_\text{TOTAL} = 30/100$.
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Figure 3. SEM micrographs at high magnification of SnO₂:F thin films deposited at 450°C, from starting solutions with different water content. (a) $\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 2.5/100$; (b) $\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 10/100$; (c) $\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 20/100$; and (d) $\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 30/100$.

In Figure 2, at low magnification, it can be seen that SnO₂ films deposited with the lowest water content ($\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 2.5/100$, Figure 2(a)), a few secondary grains in the order of 1.5 μm are formed on the compact and uniform surface of the film; in the case of films deposited from a solution with a higher water content ($\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 10/100$, Figure 2(b)), the number of secondary particles decreases both in number and size, whereas for the highest water content ($\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 30/100$, Figure 2(d)) no particles can be observed. From a higher zoom of the images it shows that grains of films deposited from solutions with the lowest water content present irregular size and shape, then it can be considered that grain size is ranging from 100 to 200 nm (Figure 3(a)). The surface of films deposited with a higher water content ($\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 10/100$) show an increase in the size, higher than 200 nm, and the geometry of the grains resembles a cylinder-shaped form (Figure 3(b)). The films deposited with a water content of 20/100 show a surface covered by triangular pyramids with irregular size, in the order of 150 nm (Figure 3(c)). Finally, the films deposited with the highest water content, 30/100, shows well-defined triangular pyramids with small dimensions compared with films deposited from a starting solution with a water content of 20/100 (Figure 3(d)).

3.4. Optical Properties

Figure 4 shows the optical transmittance spectrum of a SnO₂:F thin film deposited from a starting solution containing the highest water content, 30/100, measured in the wavelength range from 300 to 1000 nm, taking the air as reference. All SnO₂:F thin films were highly transparent in the visible range, with an optical transmittance in the order of 80% at the middle of the visible range (550 nm). The optical band-gap values, $E_G$, were determined according to Roth and Webb procedure [20], for heavily doped semiconductors, and from the absorption coefficient spectra $\alpha(\lambda)$ computed from the Burguer-Lambert equation ($I = I_0 \exp(-\alpha d)$), where $\alpha(\lambda)$ is the absorption coefficient, and $d$ the film thickness [21]. A typical band gap calculation is reported in the inset in Figure 4, corresponding to the SnO₂:F sample deposited from the starting solution with the highest water content, namely, $\text{Vol}_{\text{H}_2\text{O}} / \text{Vol}_{\text{TOTAL}} = 30/100$.

In general, $E_G$ values were high, around 3.9 eV, irrespective of both water content in the starting solution and deposition temperature. This band gap increasing can be interpreted according to the Moss Burstein effect, which states that the increase in the free carrier concentration,
due to the high doping level, fills empty states belonging
to conduction band, increasing the energy magnitude
required for the valence band to conduction band transi-
tions.

3.5. Chemical Composition

Compositional analysis of the elements present in the
films was performed on selected samples. Figure 5
shows the EDS measurement of a SnO$_2$:F thin film de-
posited at 450°C, from a $\text{Vol}_{\text{H}_2\text{O}}/\text{Vol}_{\text{TOTAL}} = 30/100$
starting solution. Films are almost stoichiometric, with a
Sn:O ratio of 1:2, found in all the films. However, the
non-intentional incorporation of undesirable elements
was also confirmed by EDS analysis, as Ca, Si, K, Mg
were detected in all the samples.

![Figure 4. Optical transmittance SnO$_2$:F thin films deposited at 450°C, from a $\text{Vol}_{\text{H}_2\text{O}}/\text{Vol}_{\text{TOTAL}} = 30/100$ starting solution.](image1)

![Figure 5. EDS measurements of SnO$_2$:F thin films deposited at 450°C, from a $\text{Vol}_{\text{H}_2\text{O}}/\text{Vol}_{\text{TOTAL}} = 30/100$ starting solution.](image2)
These elements come from the glass substrate due to exo-diffusion of impurities during the growth process, and are responsible of the increase in the electrical resistivity of the films. It is worthy of mention that nitrogen element was also detected into the lattice, although in a small quantity as compared with alkaline elements. It is hard to assume that nitrogen can dope the SnO$_2$ films effectively due to the fact that a low electrical resistivity was obtained. In this case a more careful study has to be done in order to figure out the specific sites where nitrogen is hosted. Fluorine was detected into the films and a variation ranging from 4 to 4.5 at% was measured. This value of fluorine atomic content into the SnO$_2$ lattice is consistent with other reported [22], however, there still remain the question about specific sites where F is incorporated, as clustering of fluorine or grain boundary segregation can occur.

4. Conclusion

The characteristics of SnO$_2$:F thin films deposited by ultrasonic spray pyrolysis (USP) as a function of both water content in starting solution and substrate temperature were studied. The minimum electrical resistivity and maximum optical transmittance in the UV-visible region were studied. The minimum electrical resistivity and maximum optical transmittance in the UV-visible region was achieved for SnO$_2$:F thin films were around $8 \times 10^{-4}$ $\Omega$cm and 75%, respectively. According to the results obtained, SnO$_2$:F thin films deposited by USP can find application as transparent electrodes in organic thin film solar cells due to both the low resistivity measured and high chemical stability presented.

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