Study of TiO₂, SnO₂ and nanocomposites TiO₂:SnO₂ thin films prepared by sol-gel method: Successful elaboration of variable-refractive index systems

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Abstract
In this research TiO₂, SnO₂ and TiO₂:SnO₂ nanocomposite thin films were fabricated by the sol–gel dip coating technique. The mixture was prepared by varying the molar ratio of SnO₂ to TiO₂, i.e. TiO₂:SnO₂ (9:1), TiO₂:SnO₂ (8:2) and TiO₂:SnO₂ (6:4)). The obtained samples were characterized by means of the Raman microscopy, Scanning Electron Microscopy (SEM), UV–Vis spectrophotometry and m-lines spectroscopy (Prism coupler). Raman analysis shows that pure TiO₂ and SnO₂ thin films are characterized by the vibrational modes of anatase and rutile cassiterite, respectively. Furthermore, the Raman spectra of the TiO₂:SnO₂ nanocomposites show the presence of a mixture of anatase and rutile TiO₂ phases. The SEM images reveal that the morphology is clearly modified with SnO₂ content. The ripples in the transmittance spectra decreased with increasing SnO₂ content. Also, the evolution of the optical band gap seems to be consistent with the Raman analysis. A great attention has been paid to the refractive index measurements by the prism coupler technique. In this way, variable–refractive index systems have been successfully obtained using TiO₂:SnO₂ nanocomposite thin films.

1. Introduction

TiO₂ and SnO₂ oxides have several advantageous properties such as availability, good thermal stability, low cost, easy to elaboration, good acid resistance, high band gap compared to traditional semi-conductors (3–4 eV) [1, 2] and excellent optical quality. These properties make them attractive materials for several applications such as antireflective coating, optical filter, planar waveguides and solar cells [3–9].

Owing to the numerous published papers on pure transparent conducting oxide (TCO) thin films [2, 10], it is necessary to develop other works which could be devoted to change and enhance the properties of these films using new different approaches. The formation of multi–oxide systems or nanocomposites is one of the most important approaches despite the few works devoted to this domain. Recently, some studies have reported the mixing of TiO₂ with various metal oxides such as the coupling of TiO₂ with SnO₂ which has attracted a particular attention. According to the literature, the studies of TiO₂:SnO₂ are mainly devoted to gas sensors and photocatalytic applications [11]. Very few works deal with the detailed evaluation of the physical properties, in particular the optical and the structural ones. For example, as suggested by Sönmezoglu et al [12], SnO₂ can accelerate the anatase-to-rutile phase transformation in TiO₂:SnO₂ nanocomposites prepared by the sol-gel method due to the similarities in rutile structures. They have also reported the effects of film thickness on the optical properties where the transmission spectra are analyzed by the Swanepoel’s envelope method and the optical parameters such as the refractive index, the extinction coefficient and the dielectric constant are deduced. Again, the optical band gap values are calculated by Tauc model and W–D model.
In the present study, TiO$_2$, SnO$_2$ and TiO$_2$:SnO$_2$ nanocomposite thin films were prepared by the sol-gel dip coating method; the structural, morphological and optical properties were studied. In particular, the originality of this work is the successful elaboration and characterization of Variable–Refractive index systems by the Prisme Coupler technique since there are no reports to the best of our knowledge on this subject.

2. Experimental

Sol–gel is based on the hydrolysis and condensation of metal alkoxides. The general composition of these alkoxides is $M(O-\text{R})_n$, where R is an alkyl radical. The precursor alkoxides have then to be stabilized and controlled in order to obtain high quality thin films.

The used precursor for preparing titanium solution is titanium isopropoxide (Ti(OCH(CH$_3$)$_2$)$_4$) which was dissolved in isopropanol. The solution was left under closed stirring during 10 min. Then, acetic acid was poured to stabilize the sol and generates water by homogeneous esterification reaction with isopropanol. The solution is stirred during 15 min. Finally, methanol was added and stirred during 2 h. Tin oxide solution was prepared by dissolving tin chloride dihydrate precursor (SnCl$_2$.2 H$_2$O) in ethanol (C$_2$H$_5$OH) and stirring for 10 min at 60°C. Then, acetic acid was added. The obtained solution is stirred for 2 h. The composite sols were then prepared by mixing TiO$_2$ and SnO$_2$ solutions with different molar ratios (mol. %) of SnO$_2$ to TiO$_2$ (TiO$_2$:SnO$_2$ (9:1), TiO$_2$:SnO$_2$ (8:2) and TiO$_2$:SnO$_2$ (6:4)) followed by stirring at room temperature for 1 h.

Thin films were deposited on glass substrates. Prior to deposition, the glass substrates were ultrasonically cleaned with ethanol for 3 min, then rinsed with distilled water and dried. The substrates were dipped into the solutions and were pulled up at a constant rate of 10 cm min$^{-1}$. Then, each layer was dried for 15 min. SnO$_2$ and TiO$_2$ samples were composed of 15 and 5 layers respectively. Concerning TiO$_2$:SnO$_2$ nanocomposite, the number of deposited layers was fixed at 5. Finally, all samples were annealed at 500°C in air for 1 h.

The Raman spectra were recorded using a Renishaw invia Raman microscope equipped with a motorized xy stage and autofocus. The observation of surface morphology was carried out using FEI Quanta 950 model Scanning Electron Microscope. Transmission spectra were recorded using Shimadzu UV2401PC Uv-Vis spectrophotometer. The waveguiding properties were investigated by a Metricon. 2010/M prism coupler. A right-angle rutile prism $P_2$ ($n_{TE} = 2.8639$, $n_{TM} = 2.5822$) was used for coupling light of a He–Ne laser at a wavelength $\lambda = 632.8$ nm into the waveguide.

3. Results and discussion

3.1. Raman Analysis

Raman patterns of the samples of TiO$_2$, SnO$_2$ and TiO$_2$:SnO$_2$ are shown in figure 1(a), (b). Raman spectrum of TiO$_2$ thin films shows the vibrational bands characteristics of TiO$_2$ anatase phase localized at 145 ($E_g$), 197 ($E_g$), 399 ($B_{1g}$), 514 ($B_{1g}$) and 639 ($E_g$) cm$^{-1}$. The Raman spectrum of SnO$_2$ thin films is characterized by the classical vibrational bands observed at 474 ($E_{g1}$), 632 ($A_{1g}$) and 780 ($B_{2g}$) cm$^{-1}$ assigned to SnO$_2$ rutile structure (cassiterite) [13]. Ferreira et al [14] attributed the vibrational hump localized at 130 cm$^{-1}$ to non degenerated $B_{1g}$ mode of SnO$_2$ which is assigned to rotation of the oxygen atoms at tetragonal unit cell of rutile. Besides, we also observed other Raman peaks of 250 and 302 cm$^{-1}$ which can be assigned to optical phonon modes of
SnO$_2$ (Eu (LO) and Eu (TO)) [14, 15]. The peak localized at 558 cm$^{-1}$ is assigned to SnO surface vibrations as suggested by Yang et al. [16].

Raman spectra of the TiO$_2$:SnO$_2$ samples show the presence of a mixture of rutile and anatase TiO$_2$ phases. The emission band belonging to anatase appears at 145 (E$_g$) cm$^{-1}$, while those corresponding to rutile appear at 250 (SOE), 440 (E$_g$) and 610 (A$_{1g}$) cm$^{-1}$ [17, 18]. By increasing the molar content of SnO$_2$, the anatase peak intensities drastically decrease and the rutile peaks increase. This suggests that SnO$_2$ promotes and facilitates the growth of TiO$_2$ rutile at low temperatures, due to the similarity of the structures between SnO$_2$ and TiO$_2$ rutile phase [12, 19]. It should be noted that there are no vibrational modes characteristics of SnO$_2$. This is, probably, due to the fact that SnO$_2$ modes are overlapped by the broad humps of TiO$_2$ rutile localized at 440 (E$_g$) and 610 (A$_{1g}$) cm$^{-1}$. The similarity of the structures between TiO$_2$ and SnO$_2$ consolidates this assumption.

3.2. SEM images
SEM images of TiO$_2$, SnO$_2$ and TiO$_2$:SnO$_2$ thin films are shown in figure 2. The image of TiO$_2$ thin films (figure 2(a)) reveals non uniform and separated grains dispersed in amorphous phase. For TiO$_2$:SnO$_2$ composites (figures 2(b)–(d)), the grains size is larger with various lateral sizes and shapes. These images reflect the coexistence of anatase and rutile, where some particles are in nano and others are in micro size. The SnO$_2$ film possesses irregular facets.

3.3. UV–Visible analysis
Transmittance spectra of TiO$_2$, SnO$_2$ and TiO$_2$:SnO$_2$ thin films are shown in figure 3. The spectrum of TiO$_2$ films is characterized by ripples which can be attributed to the light interference phenomenon. The number of ripples decreases with SnO$_2$ content. These ripples disappeared in SnO$_2$ thin films indicating the influence of tin oxide on the interference phenomenon. Addamo et al [20] have attributed the observed ripples in their TiO$_2$ sol–gel films to the interference between the optical interfaces. In our study, SnO$_2$ thin films are composed of 15 layers i.e., more optical interfaces than in TiO$_2$ films which is composed of 5 layers, but no ripples are observed. In fact, the interference could occur when the object has a periodic structure (as in the case of multilayer thin films) and the thickness of the structure period (one layer) is closer to the wavelength of the incident light. In this context, a 5 layer TiO$_2$ thin film with a thickness about 30–50 nm for each layer will give rise to interference phenomenon more than a 15 layers SnO$_2$ thin film with a thickness about 5–10 nm for each layer.

However, the homogenous roughness in the surface–air, layer–layer and layer–substrate interfaces can also influence the interference. We believe that the roughness in the optical interfaces for TiO$_2$ thin films is more important than that of SnO$_2$ and TiO$_2$:SnO$_2$ mixtures, probably due to the difference in the sols viscosities.

The optical band gap E$_g$ of the films is calculated using Tauc relation [21]:

$$\alpha h\nu = A(h\nu - E_g)^m$$

Where $\alpha$ is the absorption coefficient, $h\nu$ is the photon energy and $m$ is a factor governing the transition types; $m = 1/2$ for a direct gap such as SnO$_2$ and equals to 2 for an indirect band gap semiconductor such as TiO$_2$ since the indirect band–band transition is the most dominant [6, 22].

In this way, TiO$_2$:SnO$_2$ composites are considered as indirect band gap semiconductor since TiO$_2$ is the major phase. Extrapolating the straight line part of Tauc plot (the inset of figure 3) gives the optical band gap energy of the materials. The band gap energies are listed in table 1. As one can see, the optical band value of TiO$_2$ is relatively higher than that reported for bulk anatase [23]. The energy band gap decreases with the increase in the SnO$_2$ content up to 20 % mol. This evolution seems to be in agreement with the Raman spectra results which exhibit a mixture of rutile and anatase TiO$_2$ phases. It is well known that TiO$_2$ rutile phase has smaller optical band gap than anatase. However, a content of 40 mol % of SnO$_2$ causes an increase in the optical band gap but it remains lower than that of pure TiO$_2$.

This could be explained by the competition between TiO$_2$ rutile and SnO$_2$ rutile phases. In this way, TiO$_2$ rutile phase tends to decrease the optical band gap and SnO$_2$ phase has a tendency to increase it, since cassiterite-SnO$_2$ has a high gap value [24]. Effectively, the value of pure SnO$_2$ band gap is about 4 eV. The same results have been reported by Mahanty et al [25].

3.4. Waveguiding measurements
For the waveguiding characterization, the dark m-lines spectroscopy with a totally automated setup has been used. It is well-known that the m-lines spectroscopy is a convenient and an efficient technique of launching light into a thin film for exciting waveguide modes [26]. Figure 4 shows the recorded waveguiding modes of TiO$_2$ and TiO$_2$:SnO$_2$ samples. We observe the excitation of one guided mode for both TE$_0$ and TM$_0$ polarizations in all samples. Under the assumption of the isotropic refractive index [6, 27], the refractive index and the thickness of the samples are deduced and listed in table 2.
TiO$_2$:SnO$_2$ films are thinner than those of TiO$_2$ (the thickness decreases from 210 nm for TiO$_2$ to 164 nm for TiO$_2$:SnO$_2$ (6:4) thin films). This implies that the ratio between the viscous drag ($\mu V$) and gravity force ($\rho g$) of the mixture sol is smaller than that from TiO$_2$ sol. In fact, for high viscosity and withdrawal speed (as in our case), the thickness is balanced by the ratio between $\mu V$ and $\rho g$ as follows [28]:

$$h = C \left( \frac{\mu V}{\rho g} \right)^{1/2}$$

Where $h$ is the thickness, $\mu$ is the viscosity of the sol, $V$ is the withdrawal speed (it is constant), $\rho$ is the liquid density, $g$ is the acceleration of gravity and the constant $C$ is about 0.8 for Newtonian liquids.

The refractive index ranges from 2.10 for TiO$_2$ to 1.88 for TiO$_2$:SnO$_2$ (6:4) thin films. Normally, the thinner films are denser (less porous) than the thicker ones since the thinner films will dry and anneal more rapidly. In a

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**Figure 2.** SEM images of (a) TiO$_2$, (b) TiO$_2$:SnO$_2$ (9:1), (c) TiO$_2$:SnO$_2$ (8:2), (d) TiO$_2$:SnO$_2$ (6:4) and (e) SnO$_2$. 

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previous work, Jiag et al [29] have reported that the thicker sol–gel TiO2 films are more porous and as a consequence the refractive index increases with decreasing thickness. In our study, it is not the case, i.e., smaller thickness gives rise to a TiO2:SnO2 mixture having a smaller refractive index than thicker TiO2 thin films. Thus,

**Figure 3.** UV–Vis spectra of TiO2, SnO2 and TiO2:SnO2 thin films (the inset of figures: Tauc plots).

**Table 1.** Optical band gap values of TiO2, SnO2 and TiO2:SnO2 thin films.

| Samples            | Optical band gap (eV) |
|--------------------|-----------------------|
| TiO2               | 3.44                  |
| TiO2:SnO2 (9:1)    | 3.37                  |
| TiO2:SnO2 (8:2)    | 3.19                  |
| TiO2:SnO2 (6:4)    | 3.41                  |
| SnO2               | 4.00                  |
we believe that the reason for this behavior is SnO₂ content which has greater impact on the refractive index of sol–gel films than their porosity. In this context, the refractive index of sol–gel SnO₂ is smaller than that of TiO₂ due to the difference in the electronic polarisability; thus by mixing the two sols, the resulting mixtures should have smaller values of the refractive index. The reported values of the refractive index for sol–gel TiO₂ thin films lie in the range ∼2.00–2.20 [30, 31]. These values are consistent with our deduced value (2.10). For sol–gel SnO₂ thin films, Guglielmi et al [32] have reported a value range about 1.65–1.75. It should be noted that the excitation of the optical modes of SnO₂ layers is unsuccessful due to the small difference of the refractive index squares between SnO₂ film and glass substrate. In this context, the waveguiding is so difficult if not impossible.

Previously, Variable–Index systems are studied by McCulloch et al [33] using Silica/Titania composites (TiO₂:SiO₂) and served as optical sensors.

4. Conclusions

We have grown TiO₂, SnO₂ and TiO₂:SnO₂ nanocomposites (TiO₂:SnO₂ (9:1), TiO₂:SnO₂ (8:2) and TiO₂:SnO₂ (6:4)) thin films by sol–gel dip coating process. Pure TiO₂ and SnO₂ films are crystallized in anatase and cassiterite phases, respectively. The use of nanocomposites of TiO₂:SnO₂ induces the growth of rutile phase of TiO₂ due to the similarity of the structures between SnO₂ and rutile of TiO₂. The interference phenomenon is clearly seen in the films where the ripples in the transmittance spectra decreased with increasing SnO₂ content. The evolution of the optical band gap energy seems to be consistent with the Raman analysis. The originality of this work is the successful elaboration and characterization of variable-refractive index systems by the prisme coupler technique.

Table 2. Optic geometrical parameters of TiO₂, SnO₂ and TiO₂:SnO₂ thin films.

| Samples          | Effective index TE (±10⁻⁴) | Effective index TM (±10⁻⁴) | Thickness (±0.1 nm) | Refractive index (± 10⁻⁴) |
|------------------|---------------------------|---------------------------|---------------------|--------------------------|
| TiO₂             | 1.8770                    | 1.7399                    | 210.1               | 2.1062                   |
| TiO₂:SnO₂ (9:1)  | 1.8459                    | 1.6857                    | 200.0               | 2.0369                   |
| TiO₂:SnO₂ (8:2)  | 1.6218                    | 1.5172                    | 187.1               | 1.9354                   |
| TiO₂:SnO₂ (6:4)  | 1.5416                    | 1.4020                    | 164.3               | 1.8895                   |
| SnO₂             | /                         | /                         | /                   | /                        |

Figure 4. Optical guided modes spectra of TiO₂, SnO₂ and TiO₂:SnO₂ thin films.
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