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Synthesis and characterization of $Zn_{(x)}Sn_{(1-x)}O$ thin films deposited by pyrolysis spray method

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In the present work we prepared conducting and transparent thin films $ZnO:SnO_2$ by pyrolysis spray technique on glass substrates. These films are obtained starting from solution of zinc acetate and tin acetate dissolved in methanol, at substrate temperature T = 350 °C. Our interest is on the investigation of percentage of phase on the optical and structural properties of these films. For that we used the optical spectroscopy of transmission UV-Visible for the optical characterizations and the diffraction of X-ray for the structural characterizations of our films. UV-Visible spectrophotometer confirms that it is possible to obtain good transparent films with a transmittance from 65 to 85% in the visible. The increase in Sn increases the optical band gap. This last varies from 3. 3to 3.77 eV. The structural analysis showed that the films (ZnO and $Zn_{0.5}Sn_{0.5}O$) deposited have a preferential orientation according to the direction (002), this result confirms that the majority phase is of ZnO.

Keywords: thin films, spray pyrolysis, transmission.

Синтез та характеристика тонких плівок $Zn_{(x)}Sn_{(1-x)}O$, нанесених методом розпилення піролізом. *Besra Abdelhalim, Hafdallah Abdelkader, Harkati Brahim, Ferdi Abdelhamid, Herissi Labidi*

Досліджено провідні і прозорі тонкі плівки $ZnO:SnO_2$, отримані методом піролізу на скляні підкладки з розчину ацетату цинку і ацетату олова, розчинених в метанолі, при температурі підкладки T = 350 °C. Досліджено вплив процентного вмісту фази на оптичні та структурні властивості цих плівок. Показано, що можна отримувати прозорі плівки з коефіцієнтом пропускання від 65 до 85% у видимому діапазоні. Збільшення Sn збільшує оптичну заборонену зону. Остання змінюється від 3,3 до 3,77 еВ. Структурний аналіз показав, що обложені плівки (ZnO і $Zn_{0.5}Sn_{0.5}O$) мають переважну орієнтацію (002), цей результат підтверджує, що основна фаза складається з ZnO.

Исследованы проводящие и прозрачные тонкие пленки $ZnO:SnO_2$ полученные методом пиролизного напыления на стеклянные подложки раствора ацетата цинка и ацетата олова, растворенных в метаноле, при температуре подложки T = 350 °C. Исследовано влияние процентного содержания фазы на оптических и структурных свойства этих

пленок. Показано, что можно получить прозрачные пленки с коэффициентом пропускания от 65 до 85% в видимом диапазоне. Увеличение Sn увеличивает оптическую запрещенную зону. Последняя варьируется от 3,3 до 3,77 эВ. Структурный анализ показал, что осажденные пленки (ZnO и $Zn_{0.5}Sn_{0.5}O$) имеют преимущественную ориентацию (002), этот результат подтверждает, что основная фаза состоит из ZnO.

1. Introduction

Recently transparent conducting Oxides (TCO's) have drawn much interest in the field of optoelectronics [1].Transparent conducting oxides are the material which exhibit higher optical transmittance in visible region, low sheet resistance and higher electrical conductivity. Zinc tin oxide (ZTO) is a class of ternary oxides that are known for their stable properties under extreme conditions, higher electron mobility compared to itsbinary counterparts and other interesting properties. These materials is thus ideal for applications from, gas detector, solar cells photocatalysts, light-emitting diodes, field effect transistors and (heterojunction and homojunction) diodes [2-5]. ZnO thin films are grown by different techniques such as Spray pyrolysis, MOCVD, Sol gel, Pulsed laser deposition (PLD), sputtering, etc [6-9]. Among the various TCO's such as ZnO, SnO_2, In_2O_3, TiO_2 and CdO [10], ZnO and SnO_2 is the most promising candidate for the development of transparent conductive material.

ZnO in view of its high transmission over a wide spectral range including the useful UV-Vis region and other interesting characteristics such as low toxicity, relatively low cost, and stability in reductive chemical environments. SnO_2 is a rutile tetragonal structure with oxygen deficient n type degenerate semiconductor with wide band gap of 3.6 eV. Its high optical transparency and electrical conductivity leads to very appealing applications in spintronics device [7]. In the present work, $ZnO:SnO_2$ thin films were prepared using Spray Pyrolysis method. The influence of $ZnO:SnO_2$ content level on structural and optical properties in the composite had been studied.

2. Experimental

The samples used in this study were deposited using a device made in the laboratory. The solutions used are zinc acetate ($C_4H_6O_4Zn.\ 2H_2O$) and tin chloride ($SnCl_2$) dissolved in methanol. The spray liquid is then carried through a pyrolysis system that converts into fine droplets. These precursors were sprayed onto glass substrates placed below a substrate holder heated to a fixed temperature 350 °C.

Our focus is to study the effect of percentage of phase on the structural and optical properties of these films.

3. Results and discussion

Figure 1 shows the variation in growth rate as a function of percentage of phase X (X = 1 to 0). It is found that the growth rate of the films is high in the case of pure ZnO, but it suffices to add another oxide, the speed is reduced.

We note that the highest growth rate is that of ZnO, and then of mixing ($Zn_{0.5}Sn_{0.5}O$) and the lowest is SnO_2. This result is in good agreement with the energy of formation of the two oxides: 3.6 eV (ZnO) and 6 eV (SnO_2) [8]. In fact, the oxide which has the lowest formation energy than the highest growth rate.

The variation in the growth rate is due to the difference in surface reactions during deposition and to the dissociation enthalpies of each solution.

The variation in the growth rate with the percentage of phase X is mainly due to the percentage of the two phases present in the film and to the direction of growth of each phase. In the case where the two phases are equal or the direction of growth of ZnO is along the axis (002) parallel to the surface of the substrate [9].

Table 1. The experimental conditions for the deposited $ZnO:SnO_2$ thin films.

	Deposition time (min)	Distance nozzle-substrate (cm)	Substrate temperature (°C)	Solution concentration (M)	Percentage of phase (X)
Zinc acetate $C_4H_6O_4Zn.2H_2O$	5	25	3500	0.1	0.5 and 1
Tin chloride $SnCl_2$					

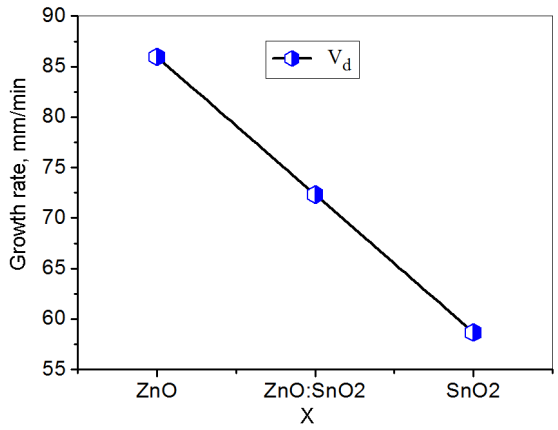

Fig. 1. Variation of growth rate with percentage of phase X.

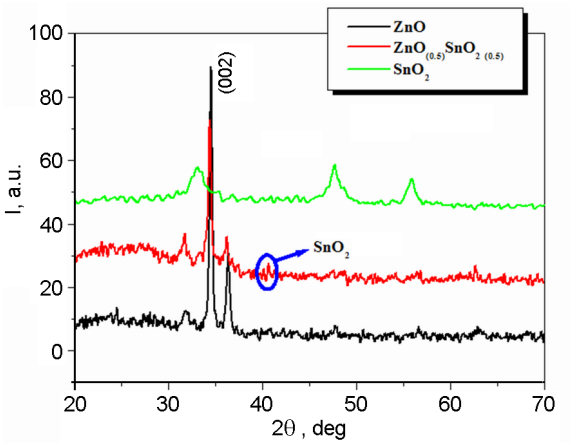

Fig. 2. XRD patterns of ZnO:SnO thin films deposited at different percentage of phase X.

We have reported, in figure 2, the X-ray diffraction spectra of the series studied (ZnO: SnO_2), for a percentage of X phase varying from 0 to 1.

Figure 2 shows the spectra of the series (ZnO:SnO_2), we note that: for high concentrations of ZnO or (X = 1 and 0.5), the peak relative to orientation (002), observed around $2\Theta = 34.5°$, is the most intense, then decreases gradually with the decrease in X to become same order as the peaks of the other orientations, it is noted that in addition to the normal direction (002) of the layer $Zn_{0.5}Sn_{0.5}O$ there is emergence of peak (210) which correspond to SnO_2. This result confirms that the majority phase is ZnO [2]. This result is in good agreement with the energy of formation of the two oxides.

As our films are made up of a binary compound, we have taken into account the simultaneous existence of two different types of grains. The average grain size for each of the two phases that coexist in our films was calculated using the scherrer formula [10]:

$$D=\frac{0.9\lambda}{\beta\cos\theta} \qquad (1)$$

For the series (ZnO:SnO_2), we used the peaks (101), (002) and (100) of ZnO and (210) respectively for SnO_2.

The results of the variation, as a function of percentage of phase X, of the grain size are presented in Figure 3.

The reduction in the size of the grains of the main phase is caused by the bursting of the crystallites of this phase and also by the emergence of other growth plans in addition to the peaks (002), (101), (100) and (210) relating to ZnO and SnO_2. The average grain size, deduced from the evolution of

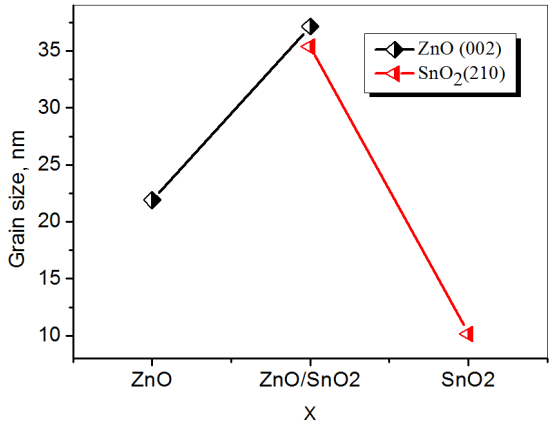

Fig. 3. Variation of grain size with percentage of phase X.

the peaks, varies from 10.17 to 37.14 nm. Note that the grain size values of our films are of the same order of magnitude as those reported in the literature [11]. With the addition of Sn, the effect of the contribution of SnO_2 increases at the expense of ZnO. For pure ZnO 21.91nm (0.8 Kcal/mol) and pure SnO_2 10.17nm (1.5 Kcal/mol). As observed in [12] and [13], there is a structural degradation of the films deposited by spray when the percentage of the mixture is high. This degradation is synonymous with the disappearance of the preferential orientation of the crystal lattice of the film.

Optical characterizations were based on transmission spectroscopy in UV-Visible. Indeed, as it was detailed in the previous chapter, the exploitation of spectra allows us to calculate the optical gap. In figure 4, the transmission spectra in the range 300 to 1100 nm are grouped together with ZnO:SnO_2 films. Although the general look

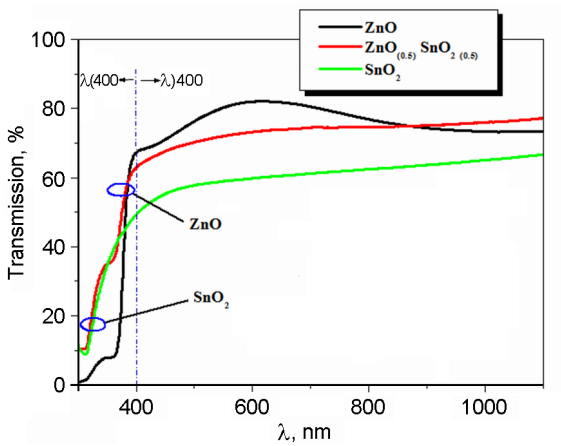

Figure 4. Transmission spectra of ZnO:SnO_2 thin films.

of the spectra is identical, these are composed of two regions:

A region of high transparency located between 400 and 1100 nm, the transmission value is around 65 to 85%. This value, reported by several authors [14-16], gives the thin layers of ZnO, $Zn_{0.5}Sn_{0.5}O$ and SnO_2, the character of transparency in the visible. In this wavelength range, interference fringes are observed in the case of pure ZnO films. These fringes, characterized by the undulations of the curves, are due to the multiple reflection of the radiation on the two interfaces of the film.

A region (λ <400 nm) characterized by a strong absorption and a low transmission of the layer which corresponds to the fundamental absorption in the films of ZnO, $Zn_{0.5}Sn_{0.5}O$ and SnO_2. This absorption is due to the electronic inter-band transition. The variation in transmission in this region is used to determine the gap.

With the addition of Sn, the effect of the contribution of SnO_2 increases at the expense of ZnO. The height of the hump increases to finally coincide with that of tin oxide as shown in figure 4. This confirms the segregation of ZnO phase and SnO_2 phases as deduced from the analysis of XRD and indicates that the films deposited have a heterogeneous structure composed of ZnO and SnO_2 separate phases [15].

From the region of fall of the transmittance (~ 400 nm), we deduced the optical gap of our films. The latter is estimated from the intersection of the curve giving $(\alpha h\nu)2=f(h\nu)$ with the abscissa [2].

In figure 6, we have reported the variation of the optical gap of the ZnO, $Zn_{0.5}Sn_{0.5}O$ and SnO_2 films as a function of percentage of phase X.

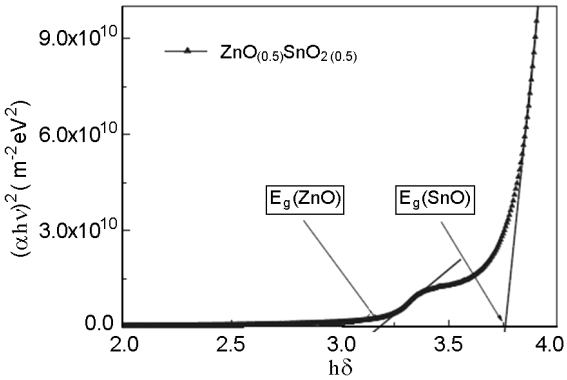

Fig. 5. Typical variation of $(\alpha h\nu)2$ as a function of photon energy ($h\nu$).

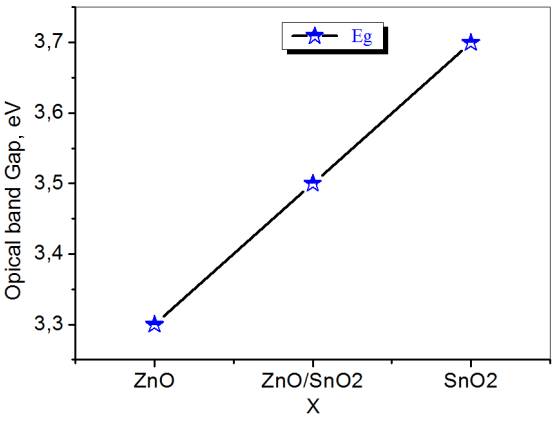

Figure 6. Variation of optical band gap with percentage of phase X.

As we can see the gap of ZnO (3.3 eV) and smaller than that of SnO_2 (3.7 eV). Since the processing of the X-ray spectra gives us two separate phases, and the optical characterization gives us a superposition of two spectra; one of ZnO and the other of SnO_2 (X = 0.5), the addition of another oxide (SnO_2) to ZnO tends to increase the gap. Indeed, it is well known that the variation of the gap is mainly caused by the concentration of free electrons (transition from Zn^{2+} to Sn^{4+}) [16-18]. So in this case, the increase in the optical gap is mainly due to the contribution of the secondary phase (SnO_2). When the concentration of the secondary phase increases, there is an increase in the concentration of free electrons which comes from this phase until it reaches the gap of this phase (SnO_2).

The variation of urbach energy with percentage of phase is plotted in figure 7. As can be seen, the addition of Sn tends to increase the disorder regardless of the percent-

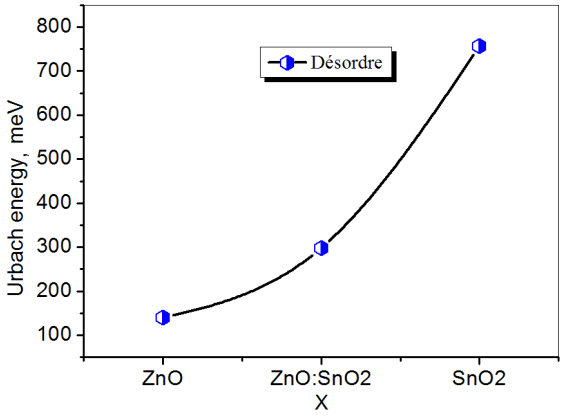

Figure 7. Variation of Urbach energy with percentage of phase X.

age. As the two oxides have small sizes and of the same order (Zn^{2+}: 0.74 Å, Sn^{4+}: 0.81 Å) [17]. It is possible that in the mixture the atoms are inserted in the interstitial sites which increase this disorder. Indeed, this increase in disorder is due to the introduction of impurities.

4. Conclusions

ZnO thin films were deposited by pyrolysis spray technique with a non aqueous solution. The effect of percentage of phase X on the structural and optical properties of films was investigated. The structural study of films by XRD shows, from the peaks of the spectrum, that the films (ZnO and $Zn_{0.5}Sn_{0.5}O$) deposited have a preferential orientation according to the direction (002), this result confirms that the majority phase is ZnO. The UV-Visible spectrophotometer confirms that it is possible to obtain good transparent films with a transmittance of 65 to 85% in the visible. The band gap energy values are determined from the transmission spectra. They are found from 3.3 to 3.77 eV. The increase in the width of the forbidden band with the percentage of phase due to the increase in free carriers. The increase in urbach energy results in the increase in structural disorder.

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