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Al Concentration Effect on ZnO Based Thin Films for Photovoltaic Applications

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Abstract

In this work, we prepared aluminum-doped (Al) zinc oxide (ZnO) thin films using the sol-gel method, glass substrates have been used with zinc acetate as cations source and 2-methoxiethanol as solvent. The obtained experimental results show that the ZnO deposited films are relatively uniform. Optical measurements demonstrate that the deposited ZnO layers have a band gap of 3.26eV which is close to that of the monocrystalline ZnO, about 3.3eV. It was found that the roughness decreases by increasing the dopants concentration. Whatever the used substrate, transmission was observed between 75% and 99% for films deposited on ZnO:Al. Robust solar cells can be performed using from this study.

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Keywords: thin films, band gap, semiconductor, photovoltaic,

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1. Introduction

In the last decades, the development of thin films materials has contributed to the expansion of electronics and optoelectronics performance, including the lowering of the component cost by a mass production. Thin films can be produced from a wide range of compositions such as conductive materials, insulators, semiconductors and polymers [1-3]. There is a family of oxides which, in addition to being transparent, can become conductive (n-type) if it has an excess of electrons in their network. This excess of electrons can be created either by structural defects inducing an imbalance in the stoichiometry of the oxide, or by an appropriate doping [4]. These oxides are called, transparent

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conductive oxides (TCO). They have a high gap, actually they are a degenerated semiconductors, i.e. their Fermi PN level is closed to the conduction band (CB), and even within this band for the highly doped TCO. This means that the CB is already full of electrons at room temperature, making then the TCO conductors. In addition, the high gap of TCO (about 3-4eV) prevents them to absorb the photons having an energy smaller than the gap, and thus makes them transparent for the visible light. junctions were performed with the n-type TCO such as the p-$SrCu_2O_2$ / n-ZnO to construct a LED [5]. The ZnO may be a p-type semiconductor, therefore, transparent PN junctions produced whilst ZnO are possible. With antimony doping, J.M. Bean team shows a p-type character on ZnO deposited layers, which has achieved PN junction ZnO-based while its emission is near to the UV and visible [6]. Moreover, many researches are carried out on p-ZnO for LED applications [7].

Nomenclature

ZnO	zinc oxide
TCO	transparent conductive oxides
CB	conduction band
LED	Light-Emitting Diode
Al	Aluminum
AFM	Atomic force microscopy
ΔE_g	Variation of the gap
T	Temperature

2. Resistivity measurement

We will determine some properties of the ZnO:Al thin films developed by the spin-coating method. To study the influence of the concentration and the precursor on its properties, we used two doping sources $AlCl_3$ and $Al(NO_3)_3$ with different concentrations, the impact of the thermal treatment is made by annealing at different temperatures. We have obtained results for the résistance of the films after annealing of 500°C, for one hour with a film thickness of 100nm. Figure 1 shows the evolution of the ZnO:Al films resistivity as function of the Al-dopant concentration.

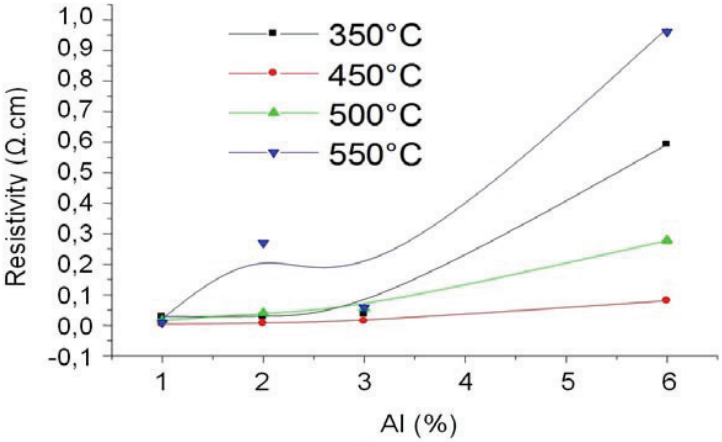

Figure 1 : Electrical resistivity of ZnO: Al films as function of dopant concentration for different annealing temperature using $Al(NO_3)_3$.

These curves show two regions of variation for the two dopants. In the first zone the resistivity decreases slowly with the Al concentration, the annealing temperature has no influence on its value which around a concentration of 2% [8-10], this decrease in resistivity with increasing the Al concentration can be explained by the increasing of the number of carriers (electrons) from donors Al_3+ ions incorporated in substitutional or interstitial positions cation Zn_2+ [11, 12].

In the second zone, whatever the annealing temperature, the resistivity increases to a significant extent with the increase of the charge carriers, the increase of the Al concentration produces an increase in the resistivity, which is probably due to the decrease of the carriers' mobility resulting from Al excess.

3. Morphological studies

The morphologies of the doped ZnO films using Al at various concentrations are shown in Figures 2 (a, b) and 3 (a, b). In both cases of the two dopants, we observed, for low concentrations of Al a smooth and homogeneous surface, by against for high doping levels; a deformation on the surface was observed which could be attributed to degradation of the film morphology as was shown by [13-15].

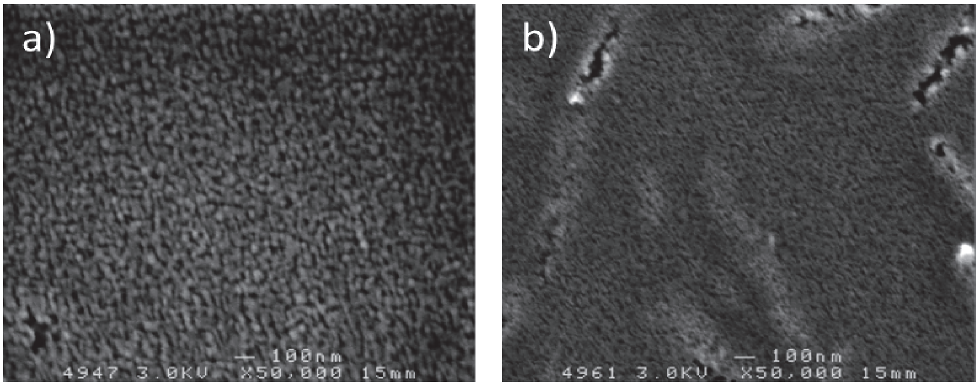

Figure 2(a,b): Morphology of ZnO:Al films for different concentrations of dopant and annealing at 450°C using $AlCl_3$: (a) 0.5%, (b) 6%.

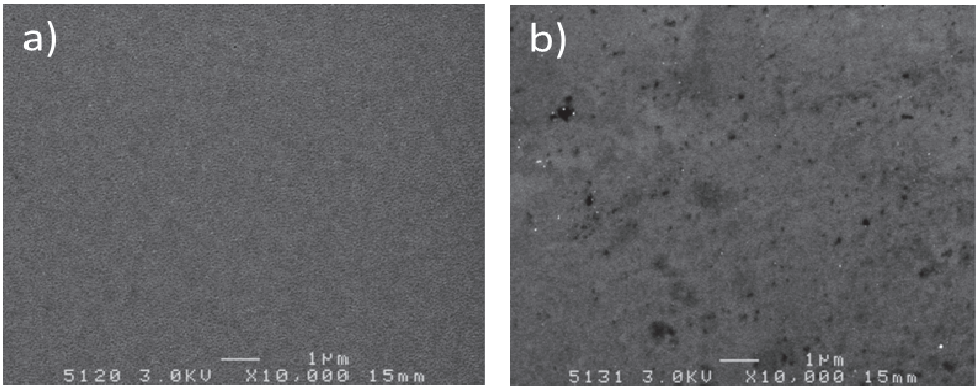

Figure 3(a,b): Morphology of ZnO:Al films for different concentrations of dopant and annealing at 450°C using$(Al(NO)_3)_3$: (a) 1%, (b) 6%.

4. Results of AFM analysis

A 3D AFM images of the surface of the Al-doped ZnO films using both doping agents $AlCl_3$ and (Al $(NO_3)_3$), are shown in Figures 4 (a, b) and 5 (a, b). The surface morphology of the films depends to the concentration of the Al, in the case of low concentration; the surfaces are homogeneous comparing to those observed with high concentration.

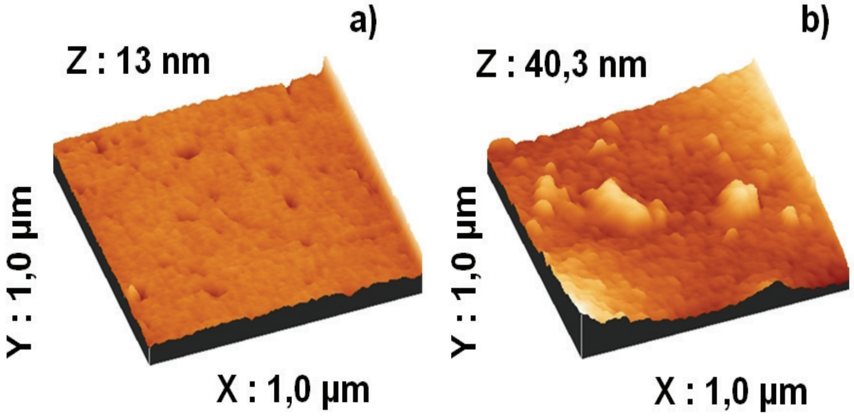

Figure 4 (a,b): AFM Images of different concentrations of dopant and annealing at 450°C using $AlCl_3$: (a) 0.5%, (b) 6%.

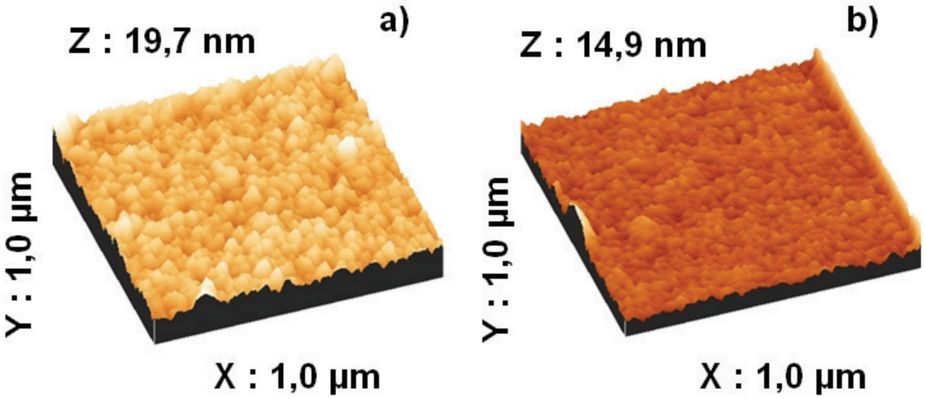

Figure 5 (a,b): AFM Images of different concentrations of dopant and annealing at 450°C using$(Al(NO)_3)_3$: (a) 1%, (b) 6%.

The roughness is reduced with the increase of the dopant concentration (Table .1) as in the case of In doped ZnO [16, 17]. This decrease can be explained by the fact that the decrease of the electric conductivity to the high doping levels may be attributed to degradation of the morphology of the film ((b) and (d)). Differences in the roughness as a function of dopant as was shown by [18], could be attributed to differences constants $AlCl_3$ and Al hydrolyzation $(NO_3)_3$, which could lead to different growth mechanisms.

5. Transmission and optical gap

The optical properties of the Al-doped ZnO thin films were determined from the transmission measurement in the range of 400-2400 nm. Figure 6 (a, b) shows the transmission spectra of ZnO with different concentrations of dopant according to the conditions of the layers deposited by the sol-gel method.

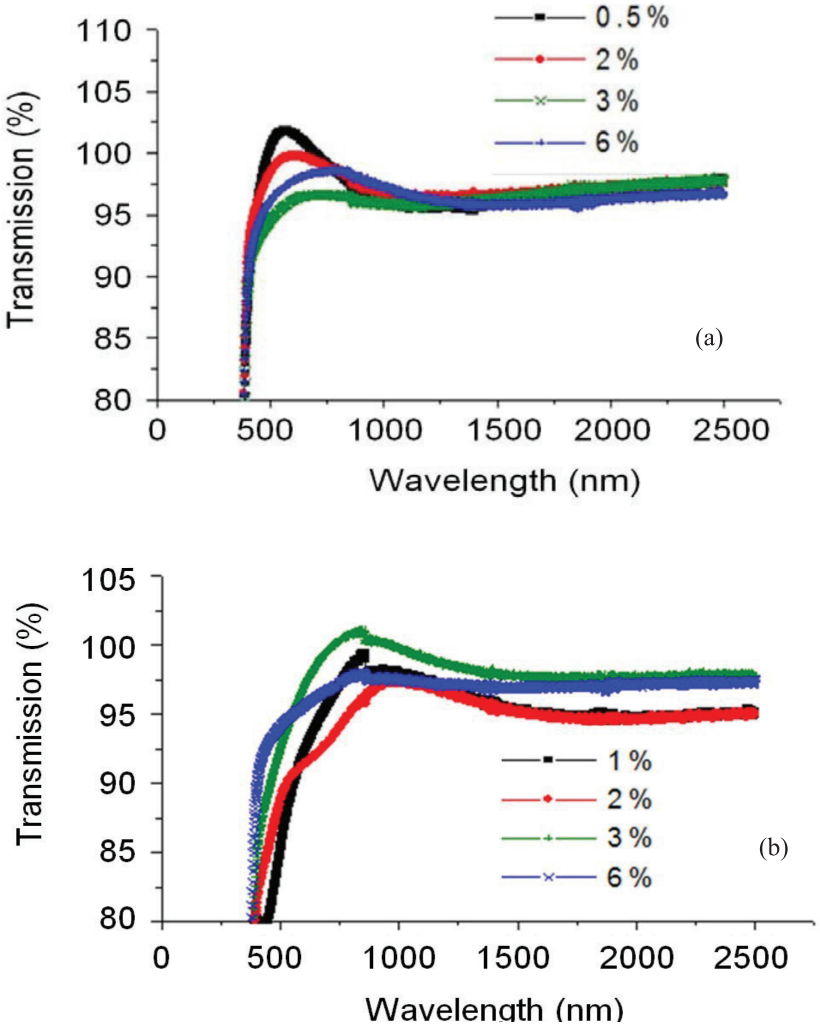

Figure 6 (a,b): Transmission spectra of ZnO: Al thin films, with annealing at 450°C and different concentrations of Al :(a) $AlCl_3$as dopant, (b) $Al(NO_3)_3$,as dopant.

All films have a very high transparency (> 90%). On the other hand, it was observed that with the increase of the doping proportion, a shift of absorption threshold towards higher energies. This discrepancy is due to the increase in the concentration of free carriers in the material blocking the lowest states in the conduction band [19-21]. These results are not significant and are consistent with the values obtained by the same method for the In-doped ZnO [16].

The shift in the absorption edge is also equal to the variation of the gap ΔE_g which is expressed by [22]. Therefore, the films were prepared with a substrate temperature of 450°C at different doping values contain a high concentration of free electrons [23] which is in perfect agreement with the change in their optical gap and electrical conductivity.

Figure 7 (a, b) illustrate the variation of $(\alpha h\upsilon)^2$ as function of the photon energy of the thin film of ZnO:Al to different concentrations of doping and annealing temperature T = 450°C, using both $AlCl_3$ doping agents and $Al(NO_3)_3$. It is clear that the dopant reduces the absorption coefficient.

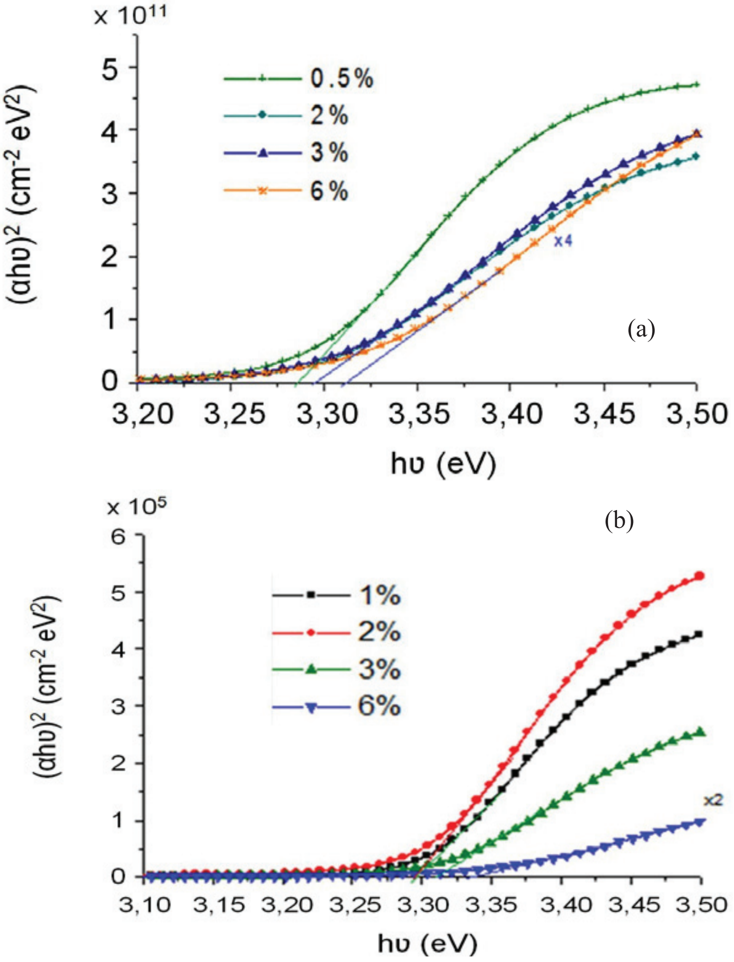

Figure 7 (a,b): Variation of $(\alpha h\upsilon)^2$ as function of photon energy for ZnO:Al film sat different doping concentrations, annealing at 450°C, (a) $AlCl_3$ as dopant,(b) $Al(NO_3)_3$as dopant.

We note that the increase in Al affects the coefficient $(\alpha h\upsilon)^2$. If Al increases from 0.5 to 6%, then the coefficient $(\alpha h\upsilon)^2$ decreases. Also Al concentration induces a change in the optical gap. The optical gap is defined by the intersection of the gradient of the curve $\alpha^2=f(h\upsilon)$ with the energy axis hυ. In figure 7.a, we examined the effect of Al films produced by $AlCl_3$ at T = 450 ° C. Then we repeated the same work with films realized by $Al(NO_3)_3$. We note that the coefficient $(\alpha h\upsilon)^2$ is more important in films achieved by $AlCl_3$ as films performed by the second component $Al(NO_3)_3$. But the optical gap constantly varies in the range [3.21-3.31] (eV).

In Table 1, we reported the values of the optical gap of the ZnO film doped with two dopants $AlCl_3$ and $Al(NO_3)_3$, and for different doping percentages. As can be seen, the addition of dopant tends to reduce the gap whatever the nature of the dopant. When the concentration of the dopant increases; the disorder increases with the optical gap, then it reduced increasingly. The values are generally between 3.08 and 3.27 eV, the optical gap values are comparable to those found in [24] and which vary between 3.31 eV and 3.21 eV. This reduction of the gap with the doping level is primarily due to distortions in the network due to the introduction of impurities (doping) and the increase of the concentration of free electrons. This is possibly the result of occupying interstitial sites in the dopant atoms because they represent the major native donor in the ZnO film [25].

Table 1 : Optical gap of ZnO:Al with annealing temperature at 450°C and for different concentrations of Al using $AlCl_3$and ($Al(NO_3)_3$) as dopant

Dopant	$AlCl_3$				$Al(NO_3)_3$			
Al (%)	0.5	2	3	6	1	2	3	6
Optical Gap(eV)	3.25	3.25	3.26	3.13	3.27	3.26	3.24	3.08

6. Conclusion

This work involves the synthesis and study of the doping of zinc oxide thin layers developed by a spin-coateur. To achieve these deposits, we used the sol-gel technique using a zinc acetate solution using, separately, the different sources of dopant ($Al(NO_3)_3$ and $AlCl_3$). It is noted for a doping of less than 2% Al resistivity decreases; thence to 2% increases considerably, by against the increase of the annealing temperature decreases. It has been shown that the roughness is reduced with the increase in concentration of dopants. The prepared samples of ZnO: Al has a transparency greater than 90% and a decrease of the optical gap. The influence of aluminum was investigated on $(\alpha h\upsilon)^2$ to an annealing temperature T = 450°C. These structures made of thin films of ZnO:Al are very useful for photovoltaic applications.

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