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Comparison of the Structural and Morphological Properties of Sn Doped ZnO Films Deposited by Spray Pyrolysis and Chemical Bath Deposition

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Abstract: The aim of this study is to compare structural and morphological properties of Sn doped ZnO films deposited by spray pyrolysis and chemical bath deposition. ZnO thin films, Sn doped or not, have been deposited by chemical bath deposition and spray pyrolysis. After deposition the films are annealed in room air, half an hour at 400°C. The films achieved are polycrystalline ZnO, with grains crystallized in the hexagonal structure. The films deposited par spray pyrolysis are homogeneous, their morphology does not vary strongly when Sn is introduced as dopant. In the case of chemical bath deposition the crystallite shapes depend significantly on the presence or not of Sn. Without Sn the grain of the films exhibit well resolved pyramidal geometry. With Sn, nanorods are clearly present in the films. This specific geometry depends on the Sn concentration. The presence of nanorods is explained by the possible catalyst effect of Sn during annealing at 400°C.

Key words: ZnO, Sn doped, spray pyrolysis, chemical bath, nanorods

INTRODUCTION

ZnO is a key technological material. It is a wide band-gap (3.37 eV) compound semi-conductor. Its high exciton binding energy (60 meV) can assure efficient excitonic ultraviolet luminescence. ZnO is transparent to visible light and can be made highly conductive by doping. After doping it is degenerated and can be used as transparent conductive oxide for electrode applications. Generally, selective elements as dopant materials in ZnO can be classified into two groups of materials. One group can substitute for Zn and the other can substitute for O. These different types of doping materials can exhibit different structural and morphological properties for ZnO due to the different treatments of Zn and O in the ZnO structure. Sn as a cation dopant can substitute for Zn. Sn can be applied as an impurity that changes the band-gap of ZnO. By alloying ZnO with another material of a

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different band-gap, the band-gap of ZnO can be fine tuned, thus affecting the wavelength of exciton emission. Whereby, the alloying of ZnO with SnO_2 creates a ZnO/SnO_2 structure, a potential candidate for future optoelectronic devices, since the addition of SnO_2, which has a larger band-gap (3.6- 3.97 eV) than ZnO, results in a widened band-gap. Several groups have applied Sn-doping using different methods in different ZnO nanostructures (Deng *et al*., 2007; Deng and Zhang, 2008; Su *et al*., 2009). Moreover, ZnO is a versatile functional material that has diverse group of growth morphologies (Wang, 2004). It can be achieved in thin film form by different techniques such as rf-magnetron sputtering, chemical vapour deposition, transport phase vapour, spin coating, chemical spray pyrolysis, chemical bath deposition (Ozgur *et al*., 2005). Chemical Spray Pyrolysis (CSP) and chemical bath deposition techniques (CBD) are the best chemical methods at a lower cost for the preparation of thin films with a larger area. Also, they provide an easy way to dope any element in a ratio of required proportion through the solution medium. These methods are convenient for preparing pinhole free, homogenous, smoother thin films with the required thickness (Patil, 1999).

The CBD uses a controlled chemical reaction to effect the deposition of a thin film by precipitation. In the most typical experimental approach, substrates are immersed in an alkaline solution containing the chalcogenide source, the metal ion and added base (Drici *et al*., 2004).

In the CSP technique, various parameters like air pressure, deposition rate, substrate temperature, distance between nozzles to substrate, cooling rate after deposition affect the physical, electrical and optical properties of the thin films. The film properties are sensitive not only to their structure but also to many other parameters including thickness, surface states, morphology etc. (Patil and Kadam, 2002).

In this study we compare the structural and morphological properties of pure and Sn doped ZnO thin films deposited by Chemical Spray Pyrolysis (CSP) and Chemical Bath Deposition (CBD).

MATERIALS AND METHODS

Pure and Sn doped ZnO thin films were prepared at the University of Lomé, in Togo (December, 2009). The characterizations have been performed at University of Nantes, France (January, 2010).

ZnO thin films and nanorods have been prepared by both a chemical spray pyrolysis methods and chemical bath deposition method. The substrates used were bare glasses. Before deposition, the substrates were cleaned by acetone for eliminating any greasy track and then they were cleaned with soap and abundantly rinsed with distilled water. Finally they were dried by a nitrogen flow.

For chemical bath deposition, films have been elaborated from solution containing 0.1 M of zinc nitrate-6-hydrate [Zn $(NO_3)_2$, $6H_2O$]. For precipitating the zinc hydroxide [Zn $(OH)_2$], 10 mL of aqueous ammonia (0.1 mol L^{-1}), was added and the pH of resultant solution was 9. In order to dope the ZnO with Sn, $SnCl_2$ was introduced into the precursor solution. The Sn/Zn ratio in the solution was 2 or 5%. During deposition, the solution was maintained at a temperature of 60°C, while the bath was continuously stirred (Drici *et al*., 2004).

For spray pyrolysis the starting solution was 0.05 M of zinc chloride ($ZnCl_2$) in deionised water. The source of dopant was tin chloride ($SnCl_2$) with concnetration of 0, 2, 6 at.% of Sn. The substrate temperature during the deposition was around 450°C. The carrier gas was the air (Bougrine *et al*., 2005).

The crystalline structure of the films was studied using an automated step scanned Siemens diffractometer with CuKα radiation source (λ = 0.15406 nm).

The surface morphology was visualized with a JEOL type JSM 6400 F Scanning Electron Microscope (SEM). Electron microprobe analysis (EMPA) (PGT-MIX, PTS model) was used to determine the film composition (centre de micro caractérisation, Université de Nantes).

When the films are deposited by CBD, immediately after deposition the films are mainly $Zn(OH)_2$ films and they should be annealed at 400°C to be converted in ZnO films. Therefore, in order to compare the film properties in similar conditions, all the films have been submitted to an annealing of half an hour at 400°C in room atmosphere.

RESULTS

First of all, the chemical composition of the films has been measured by EPMA. This EPMA technique allows estimating oxygen, however the precision of the measure decreases with the atomic weight of element. In the precision range of the apparatus it can be said that the stoichiometry of the films corresponds to ZnO and the dopant percentage follows, roughly, the initial solutions concentration, whatever the deposition process used (Table 1).

Figure 1a and b show the X-ray diffraction patterns of ZnO thins films deposited by spray pyrolysis (ZnO_{CSP}) and chemical bath deposition (ZnO_{CBD}). The films are crystallized in the hexagonal wurtzite structure (JCPDS N° 89-1397).

It was found that all the films deposited by chemical spray pyrolysis showed preferential orientation along (002) plane, this indicates that the c axis of the crystallites is uniformly perpendicular to the substrate surface (Fig. 1a). The intensity of the peak corresponding to this orientation is maximum when there is 2 at % of Sn in the ZnO_{CSP} films.

A typical XRD diagram of a ZnO_{CBD} film doped with 2at.% of Sn is presented in Fig. 1b. It can be concluded that the ZnO crystallites are randomly oriented in these films. The same results are achieved with undoped films.

Crystallite size can be estimated from the Full Width at Half Maximum (FWHM) of the X-ray diffraction liner. The broadening of the FWHM is inversely proportional to the average crystallite size (D) as predicted by the well known Scherrer's formula the grain size D is:

$$D = \frac{K\lambda}{\beta\cos\theta}$$

where, β is the observed angular width at half maximum intensity of the peak with:

$$\beta^2 = \beta'^2 - \beta_0^2 \qquad (2)$$

where, (β') is the measured line width at half maximum and (β_0) the instrumental broadening, β_0 = 0, 16° with the apparatus used. K is dimension less number which is equal to 0.9. λ is the X-Ray wavelength (0.1541 nm for $CuK\alpha_1$), θ the diffraction angle.

Table 1: ZnO thin films composition measured by EPMA

Film	Zn (at.%)	O (at.%)	Sn (at.%)
ZnO_{SP}	53	47	-
ZnO_{SP}:Sn (2%)	52	46	2
ZnO_{CBD}	52	48	-
ZnO_{CBD}:Sn (2%)	50	48	2

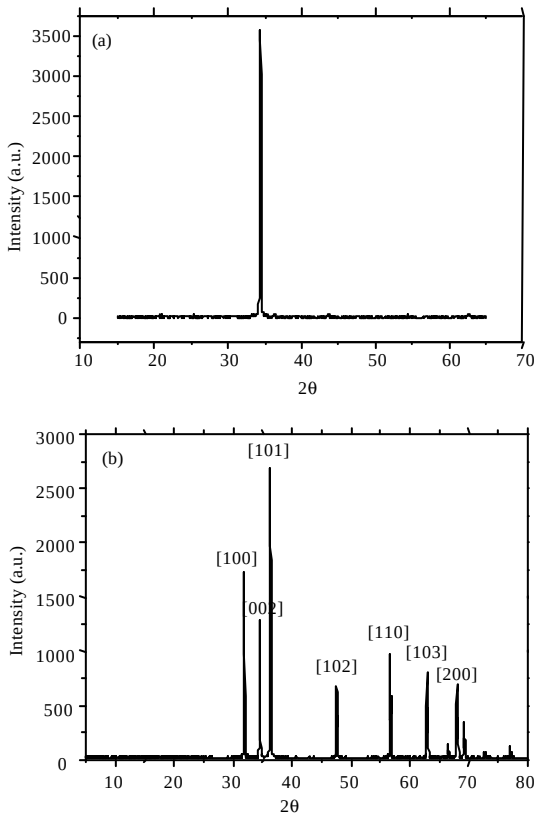

Fig. 1: XRD diagrams of ZnO thin film deposited (a) by chemical spray pyrolysis and (b) by chemical bath deposition

For the both films families the FWHM of the diffraction peaks is of the same order of magnitude than that of the apparatus. It means that we are unable to estimate the grain size. We can only say that the mean size of the crystallites is higher than 100 nm, the upper limit of sensitivity of the Scherrer's technique.

The XRD results are corroborated by the SEM study in Fig. 2a, b and 3a-c the mean grain size is higher than 100 nm. Indeed the SEM study shows that the crystallite shape depends strongly on the deposition technique. The shape of the crystallites in the films deposited by chemical spray pyrolysis is not too different with or without Sn dopant into the films, moreover the films are homogeneous. The crystallite shape is identical; it is, as expected, hexagonal. However, the crystallite diameter of the doped films (2% at. Sn) is 200 to 400 nm, while it is only 150 nm to 200 nm in the case of pure ZnO films. For higher concentration it decreases again. Such result confirms the optimal crystallisation of ZnO_{CSP} films doped with 2 at. % of tin. If these ZnO_{CSP} films exhibit quite classical morphology for polycrystalline films of material with hexagonal wurtzite structure, the morphology of the ZnO_{CBD} films is far more original. Moreover, their morphology depends on the Sn dopant concentration. The crystallites of pure ZnO_{CBD} films are well faceted with nice hexagonal surface and pyramidal shape. These pyramids are randomly oriented, which is in good agreement with the XRD study. The size distribution of the crystallites is quite broad, from 0.1 μm to more than 1 μm.

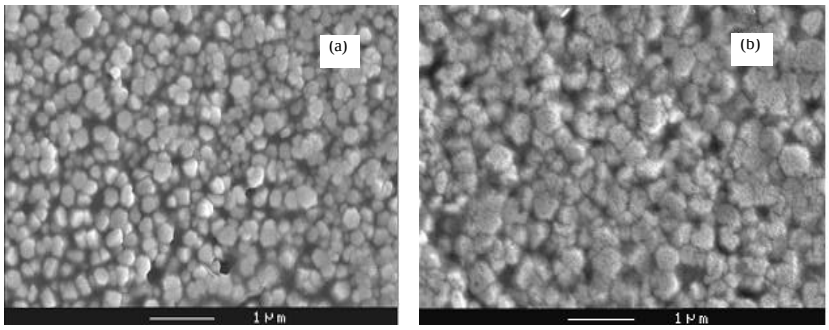

Fig. 2: Microphotographs of pure ZnO film (a) and Sn doped (2 at.%) ZnO films (b) deposited by chemical spray pyrolysis

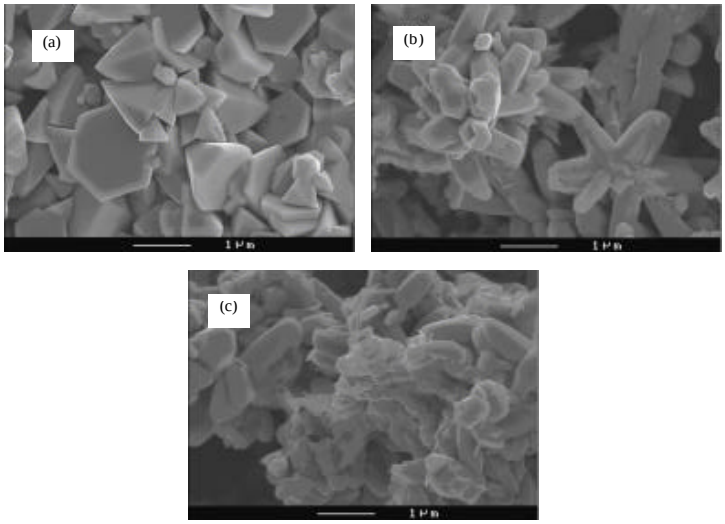

Fig. 3: Microphotographs of films deposited by chemical bath deposition: (a) pure ZnO, (b) ZnO film doped with 2 at % and (c) 5 at % of Sn

When doped with Sn the films morphology varies with the Sn concentration but they are always composed of nanorods. In the case of film doped with 5% Sn atoms, the nanorods present in the films are not as well resolved as those of the films doped at 2%. For ZnO:Sn_{CBD} with 2 at.% of Sn the films are porous with nanobrushes all over the film. In the nanobrushes, the brush stems is about 1 μm in length and 0.2-0.3 μm in diameter. With 5 at.% of Sn the films are still porous with smaller grain size (50 nm) and the features are not as well designed as those grown with 2 at.% of Sn.

DISCUSSION

First of all the EPMA, XRD and optical transmission studies show that whatever the deposition technique used and the Sn dopant concentration, the deposited films after annealing are polycrystalline ZnO films crystallized in the hexagonal structure. This result is in agreement with works of Yousefi and Kamaluddin (2009) and Chen *et al*. (2009).

However, the morphology of the ZnO films depends strongly on the deposition technique and on the doping concentration in the case of chemical bath deposition.

We will discuss these differences in the light of experimental and theoretical studies reported on ZnO nanostructured films deposited by others techniques.

A well known technique used to achieve ZnO nanorods is the vapour-liquid-solid (VLS) approach (Park *et al*., 2003). In this technique a metal catalyst is used to achieve ordered nanoraods of desired size. A liquid alloy droplet composed of a metal catalyst component and a nanowire oxide is first formed. The liquid droplet serves as a preferential site for absorption of gas phase reactant and when supersaturated, the nucleation site for crystallisation. Nanowire growth begins after the liquid becomes supersaturated in reactant materials and continues as long as the catalyst alloy remains in a liquid state and the reactant is available. During growth, the catalyst droplet directs the nanowire's growth direction and defines the diameter of the nanowire. If Au is well known as performing catalyst, it has been shown that Sn can also be used (Gao and Wang, 2002; Gao *et al*., 2003). The growth direction of the nanorods is led by the Sn catalyst, while the epitaxial growth of ordered ZnO nanorods is controlled by the substrate. The choice of a single crystal as substrate is important for epitaxial growth. The kinetic of the process is a limiting factor. The morphological difference between the films deposited by chemical spray pyrolysis and chemical bath deposition can be discussed of in the light of the VLS experiments.

In the case of spray pyrolysed films, the ZnO hexagonal structure is immediately achieved during the deposition process. The deposition rate of the film is around 1.5 nm sec^{-1}. At such velocity a process similar to that implemented in the VLS catalyst process cannot take place and the morphology of the films corresponds to classical morphology of polycrystallines films. In the case of ZnO, the crystallites have an hexagonal shape and, with or without Sn dopant, the films have similar morphology with only some difference in the crystallites size. Olvera *et al.* (2007) reported the same result by using gallium and aluminium as dopant.

In the case of CBD, after deposition the films are mainly constituted of Zn $(OH)_2$. ZnO films are obtained after annealing half an hour in room air at 400°C (Drici *et al*., 2004). Some authors have reported VLS deposition using experimental conditions (Zn source temperature and deposition duration) of the same order of magnitude than the annealing conditions used in the present study (Zhang *et al*., 2004; Lyu *et al*., 2002). It means that, in the case of doped ZnO films, the Sn present in the sample after CBD deposition can act as metal catalyst and induces ZnO nanorod growth. The film substrates are amorphous glass which justifies the high disorder of the nanorods. When the Sn concentration increases, there is a higher concentration of catalyst nucleation sites, the nanoraods diameter is smaller and the disorder higher. These results are in agreement with the works of Lee *et al.* (2006) and Gu *et al.* (2007) who observed a similar morphology with ZnO films deposed on indium tin oxide-coated glass.

CONCLUSION

ZnO polycrystalline films have been deposited by spray pyrolysis and by chemical bath deposition. Some films have been doped with Sn. The morphology of the films deposited by spray pyrolysis does not depend strongly on the Sn concentration. Hexagonal crystallites are systematically visible. For chemical bath deposition the presence or not of dopant change

strongly the film morphology. Without Sn, the films exhibit well faceted grains with pyramidal shapes. With Sn the films are constituted of nanorods, which size shape depends on the Sn concentration. The presence of nanorods is discussed in the light of VLS process. The presence of nanoraods in ZnO_{CBD} films doped with Sn, can be justified by a catalyst effect of Sn on ZnO nanorods growth.

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