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Highly doped ZnO films deposited by spray-pyrolysis. Design parameters for optoelectronic applications☆

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ABSTRACT

Synthesis and preparation of ZnO films are relevant subjects for obtaining transparent and conducting layers with interesting applications in optoelectronics and photovoltaics. Optimization of parameters such as dopant type and concentration, deposition time and substrate temperature is important for obtaining ZnO layers with optimal properties. In this work we present a study about the induced effects of deposition time on optical and electrical properties of ZnO thin films. These films were deposited by spray pyrolysis of a suitable Zn precursor, obtained through the sol–gel method. The deposition time has direct incidence on internal stress in the crystal structure, generating defects that may affect transparency and electrical transport into the layers. We performed mosaicity measurements, through X-ray diffraction, and used it as a tool to get an insight on structural characteristics and homogeneity of ZnO layers. Also, through this technique, we analyzed thickness and doping effects on crystallinity and carrier transport properties.

1. Introduction

Transparent conducting oxide (TCO) thin films have been very important concerning the design of devices with immediate applications in sensors, photovoltaics, catalysis, micro- and opto-electronics, among others [1,2]. There are several techniques that allow obtaining TCO thin films, like chemical vapor deposition [3], sputtering [4], electro-deposition [5] and spray pyrolysis [6]. The spray pyrolysis technique possesses important advantages, if compared to others, because it is quite easy to implement and at a relative low cost. It consists basically in subjecting a substrate to a controlled atmosphere where a suitable liquid precursor is sprayed or atomized. If this substrate is maintained at an adequate temperature, a series of chemical reactions is developed, promoting the deposition of a thin film onto it. The stoichiometry of the deposited material is given by the composition of the precursor solution and the chemistry of the reactions that take place. In this way, the chemical composition of the deposited layers can be precisely controlled and the feasibility of simultaneously spraying several precursors gives rise to a broad spectrum of possibilities. The precursors can be obtained *via* the sol–gel method, which allows for an easy control on chemical composition of the final layers. Therefore, the combination of sol–gel and spray pyrolysis methods provides a tool for designing TCO thin films with optimal properties to be used in diverse fields.

Among the most studied materials for TCO thin films we have chosen intrinsic and doped ZnO, since its physical, electro-optical, piezo-electrical and luminescent properties make it appropriate for a wide range of applications [6–8]. Al-doped ZnO (AZO) in the form of thin films is one of the most studied TCO materials, since it exhibits distinct advantages like abundance in nature, non-toxicity and stability, among others [9].

In previous works we have found that film microstructure strongly influences carrier transport [10,11] by analyzing and correlating variations of structural characteristics induced by thickness or extrinsic dopant effects. Some authors have reported temperature, dopant and thickness effects on the electronic and optical properties of ZnO layers [12,13]. These authors reported structural changes and morphological modifications of the layers caused by thickness increase and dopant effects, but without making emphasis in important issues like crystalline disorder or mosaicity of the films during TCO growth and nucleation processes. Therefore, our proposal is to study the growth process by analyzing the evolution of mosaicity through X-ray diffraction (XRD) measurements of the films as a function of deposition time and dopant concentration. In this work we combined the sol–gel and spray pyrolysis methods to deposit AZO films with different thicknesses, varying deposition time and dopant concentration. In this context, we investigated the effect of film thickening and dopant concentration on the evolution of morphological, electrical and optical properties. The correlation between structural properties, mosaicity and optical and electrical

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properties of the films is discussed. The results presented in this work are particularly interesting for the future development of porous silicon/doped ZnO heterojunctions for optoelectronics applications and sensing devices.

2. Experimental details

For synthesizing the AZO and ethoxylated precursors we used the sol–gel method of Zn salts [Sigma-Aldrich 99.999% $Zn(O_2CCH_3)_2(H_2O)_2$, 0.2 M] and Al dopant [14]. In this case, the Al source was the $AlCl_3 \cdot 6H_2O$ compound (Sigma-Aldrich 99.0%). The Zn salt was diluted in a mixture of deionized water and ethanol in a 1:9 proportion to get a 0.2 M solution and an equivalent concentration of triethylamine [TEA, Sigma-Aldrich >99% $C_6H_{15}N$] was added to the mixture to act as a chelating agent. Dropwise addition of acetic acid (CH_3COOH) was required to stabilize the pH (at ≈7) and avoid precipitation.

We carried out two different experiences, maintaining always a substrate temperature of 450 °C during deposition. First we varied the dopant concentration in the range between 0 and 1.5 at.% by controlling the ratio Al/Zn in the stock solution. It is worth noting that these concentrations correspond to the precursor in solution, while the actual Al concentration in the films might be lower. However, as can be seen in Ref. [15], for Al concentrations below 2 at.% the expected dopant concentration in the film should not differ considerably from that in solution.

As a second experience we fabricated samples with different thicknesses, for which the deposition times were varied in the range from 5 to 30 min (namely 5, 15, 20, 25 and 30 min). These times led to films with thicknesses of 0.43, 0.67, 0.80, 1.26 and 1.44 μm, respectively. Also, we have deposited these TCO films onto porous silicon substrates (see the synthesis and deposition details in [16]) to produce heterojunction devices. TEA was again used as an additive in the sol–gel process. The precursors were gauged in a total volume of 100 mL by using solvents like ethanol and water [17].

We performed XRD measurements in the typical θ–2θ Bragg–Brentano configuration to have an insight on the structural characteristics of the samples. In this way, we looked for the presence of ZnO characteristic diffraction peaks to ensure that crystalline domains existed in the films. We have normalized XRD patterns to account for thickness differences between samples. Structural mosaicity, or tilting between crystalline domains (as detailed in Ref. [18]), was also determined from XRD measurements. For this, the incidence angle was varied (rocked) in 2° steps around the typical incidence angle of a certain diffraction peak, given by $\theta_{hkl} = 2\theta_{hkl}/2$ for that particular peak, where (hkl) are the Miller indices of the corresponding diffracting plane. For each 2° rocking step of the incidence angle, the diffracted X-ray intensity is scanned in 2θ, as usually, around the maximum of the selected peak, *i.e.* centered at (θ_{hkl}, $2\theta_{hkl}$). This configuration and procedure has been reported by Marty et al. [19] and we have also described it in Ref. [18]. The obtained diffraction patterns were subsequently integrated over the scanned range in 2θ to construct the rocking curves as a function of $\Delta\theta$ ($=\theta - \theta_{hkl}$), whose width measures directly the degree of mosaicity or overall tilting between crystalline domains. The XRD measurements were carried out in a SHIMADZU XD-D1 diffractometer, operating with the Cu Kα line ($\lambda = 1.541$ Å).

Film thicknesses were estimated from the interference patterns of the direct transmittance spectra of the samples, measured in a Shimadzu UV3600 spectrophotometer, and were corroborated from measurements performed on scanning electron microscopy images. Surface root-mean-square roughness and texture were inspected by atomic force microscopy (AFM) measurements, in a NANOTEC probe system. In turn, for the electrical characterization we performed measurements of conductivity as a function of temperature under vacuum and Hall effect at room temperature by the Van der Pauw method. The electrical behavior of the heterojunction was determined by measuring the characteristic current–voltage (J–V) curves using a Keithley 6487 digital picoammeter (see more details of this setup in [16]).

3. Results and discussion

3.1. Doping effect

In Fig. 1 we show the XRD patterns obtained from the deposited AZO samples. For these layers, the characteristic peaks of the hexagonal ZnO structure could be observed. A strong orientation in the [0 0 2] direction was evidenced for all Al concentrations, with a texture coefficient (TC) of $TC(002) = (2.5 \pm 0.3)$ against $TC(hkl) = (0.25 \pm 0.08)$ for the other crystalline directions. Texture coefficients were calculated as in Ref. [20]. All peaks appeared at the positions corresponding to the wurtzite structure (JCPDS card No. 36–1451) but with differing relative intensities with respect to the powder pattern. We have marked with an asterisk (*) the peak centered at $2\theta \approx 30°$, present in all patterns, which corresponds to the [0 4 4] crystalline direction of a secondary zinc oxo-acetate phase [$Zn_4O(CH_3COO)_6$] [21,22]. The inset of Fig. 1 shows a detail of the XRD patterns for $31° < 2\theta < 37°$, where a shifting of the (0 0 2) peak to higher angles and an increment of the relative intensity of the peak (1 0 1) can be appreciated as the Al concentration increased.

These facts evidence a change in the ZnO structure, since a shifting of the diffraction peaks to higher angles is generally attributed to a diminution of lattice parameters. A shifting of the (0 0 2) peak from $2\theta = 34.1°$ to 34.52° was observed as the Al concentration increased. This was attributed to a variation of the lattice parameters in the ZnO crystalline structure, and the analysis was made through the equation

$$\frac{1}{d_{hkl}^2} = \frac{4}{3}\frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2}, \quad (1)$$

where (hkl) describe the crystalline planes, $a = b$ and c stand for the lattice parameters of the hexagonal ZnO structure and d_{hkl} is the characteristic distance between (hkl) planes. In this way, we found that the parameter a decreased from about 3.26 to 3.23 Å while c diminished from 5.21 to 5.18 Å, as shown in Table 1. These variations were attributed by Lin et al. to the presence of Al^{+3} ions (with lower radii) that occupy Zn^{+2} sites in the ZnO crystalline structure [23].

In Table 1 we also present the calculated values of crystallite size for each Al concentration in the deposited films. Crystallite size was

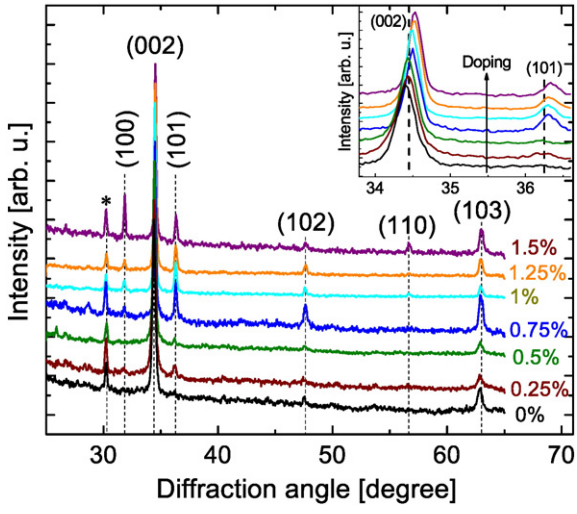

Fig. 1. X-ray diffraction patterns of AZO layers with different Al concentrations in the precursor solution. The characteristic peaks of ZnO can be observed, except for the peak marked with * that corresponds to a different phase. The vertical lines indicate the peak positions of the reference ZnO powder pattern. The inset shows the (0 0 2) peak shifting.