Characterization of thin coatings based on ZnO for photonic applications

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We present a comparison between zinc oxide films made by sol-gel dip-coating and spray-pyrolysis to be employed in opto-electronic applications. Grain size, shape, roughness, thickness, band gap, composition, crystalline orientation, electrical resistivity, and optical guided modes were evaluated by AFM, SEM, EDS, optical transmittance, electrical resistance, and end-fire coupling method, respectively. From these results, it was determined that dip-coated film is thinner (with a thickness of about 130 nm) than the spray-pyrolysis one (of about 500 nm), whereas the former showed lower roughness and higher electrical resistivity. Furthermore, a 532 nm continuous laser was coupled across the sprayed film because of its greater thickness. We conclude that the studied techniques can be complementarily implemented to obtain high-performance coatings for photonic applications, combining the lower roughness of dip coating and the wider thickness of spray-pyrolysis films.

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1. Introduction

ZnO is a wide-bandgap semiconductor of the II-VI semiconductor group. The native doping of the semiconductor due to oxygen vacancies or zinc interstitials is n-type. This semiconductor has good transparency in the visible region of the electromagnetic spectrum, high electron mobility, wide bandgap, and strong room-temperature luminescence. Those properties are valuable in emerging applications for: transparent electrodes in liquid crystal displays, energy-saving or heat-protecting windows, and electronics as thin-film transistors and light-emitting diodes [1]. For photonic components, low roughness, high transparency and a thickness of about 1 μm is desired [2].

Sol-gel process for ZnO thin films manufacturing has some advantages over other techniques like chemical vapor deposition, chemical bath deposition, reactive sputtering and pulsed laser deposition, among others. It has a lower cost and allows the tuning of refractive index, thickness, morphology of the films by varying synthesis parameters [3]. In this sense, it can be found many papers that report the characteristic of coatings manufactured by sol-gel spray-pyrolysis (SP) and dip-coating (DC), separately [3-6]. However, the characteristics of the obtained coatings depend on different parameters including temperature, composition, and ageing of the solution that lead to different grain shape and crystalline orientation [5, 7]. Then, the differences depending on physical processes playing a role in both techniques during deposition are tough to retrieve from literature, at the best of our knowledge. This is due to the variation in aging or/and composition of starting solution employed by different authors [8]. So in this paper, optoelectronic properties of coatings obtained by SP and DC, starting from the same solution, are characterized and compared. After this, a combination of both techniques is proposed for producing high performance semicondutor plane waveguides.

2. Experimental

The coatings made by spray-pyrolysis and dip-coating were fabricated starting from a precursor solution containing zinc acetate dihydrate (ZAD), acetylacetone (AcA) as a stabilizer and ethanol as a solvent. Microscope soda-lime glass slides were used as substrates, which were previously washed with a detergent solution, ethanol, acetone and dried at 80 ºC. 5 g of ZAD were dissolved in a mixture composed of 100 mL of ethanol and 2 mL of AcA. Then, the sol was stirred for 30 min at room temperature. For SP coating, 40 mL of the solution was atomized through a conventional airbrush using pressurized nitrogen (between 150 and 200 kPa) at a rate of 350 l/h. The solution was manually atomized over a 450ºC heated soda lime glass substrate. For DC, the sample was immersed and withdrawn from the solution at

40 cm/min while it was maintained at 50°C. Then, the film was dried at 85ºC for 10 minutes. This procedure was carried out four times in order to increase the thickness. Films were finally sintered at 500 ºC for 45 min with a heating rate of 4ºC/min.

The morphology of the films was evaluated by atomic force microscopy (AFM) with a system TT AFM Workshop scanning sample surfaces with a Silicon tip in "contact mode". Optical transmittance was evaluated by UV-Vis-NIR spectroscopy (Cary 5000, Agilent Technologies). The data extracted from the spectra were compared with that obtained from software provided by "FILMETRICS" and available online, that computes a theoretical transmittance curve of a film for a set refractive index and thickness [9]. The chemical composition of the films was determined by energy dispersive X-ray spectroscopy (EDS) with a JEOL JCM-6000 system. The same instrument was employed to take images by Scanning Electron Microscopy (SEM). X-Ray Diffraction (XRD) was carried out with a BRUKER D2 Phaser instrument. To perform electrical resistance measurement a conventional voltmeter was employed. To analyze optical coupling performance, the well-known end-fire method employing a standard solid-state laser of 5 mW of output power centered at a wavelength of 532 nm, was used. Near field of guided modes were projected over a white plane surface and captured by a standard camera. Before performing coupling experiment, both faces of samples were polished up to optical quality (1/4 µm powder). To polish the cross-sections of samples, these were embedded in epoxy resin.

3. Results and discussion

Fig. 1 presents a macroscopic image of both coatings along with that of the glass substrate. At sunlight reflection, the coating manufactured by dip-coating is less colored and brighter than that of spray-pyrolysis, which looks light blue and pink. The higher brightness of the DC coating can be associated with a less rough surface.

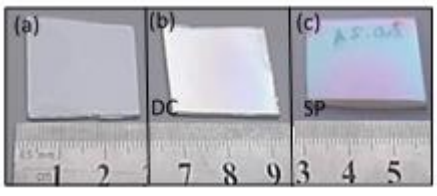

Fig. 1. Image of manufactured films (a) substrate without coating (b) dip-coated film (c) sprayed film

Fig. 2 presents the textural properties of the coatings. Grains obtained from DC are smaller (of about 50 nm and less) than those obtained from SP (of about 500 nm). Also, most SP grains have a clear dimension smaller than the other two dimensions, leading to thin hexagonal platelets with a diameter of about 500 nm. Similar grains were reported in previous works [10-12]. In contrast, for DC the grains have not a well-defined shape and they are not anisotropic. Other authors previously reported similar grains for this technique [13, 14].

The roughness of DC coatings was about +/- 25 nm and the corresponding to SP coatings was +/- 100 nm, obtained from analyzing AFM measurement presented in Fig. 2 (a) and (b), respectively. The thickness measured from the step of the film (marked as Region A in Fig. 2(a)) is shown in Fig. 2(c) and was about 200 nm for DC coating, however this method takes into account only mentioned region and its uncertainty in position from a reference level is considerably increased when the tip scans distances as long as 100 µm. In contrast, the thickness of SP coating was estimated to be of about 500 nm from SEM image shown in Fig. 2 (b). This value is in agreement with that reported by Villegas et al. [11, 12].

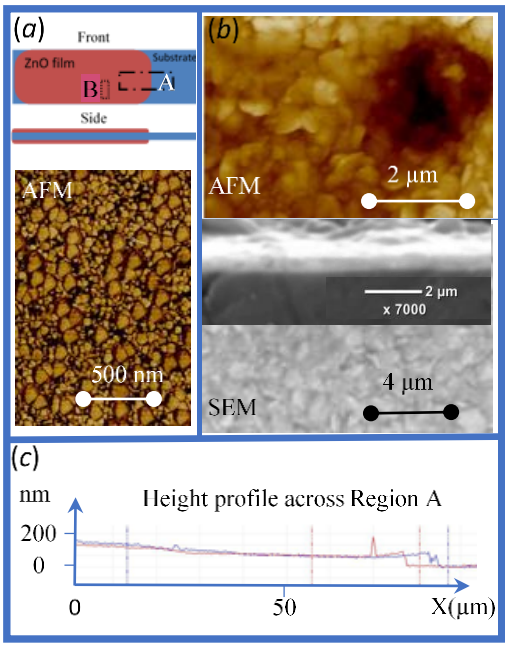

Fig. 2. (a) *Scheme of DC sample and AFM measurement over Region B. (b) Surface characterization of SP sample, and (c) Thickness of DC sample measured across the step of Region A*

The atomic composition of coatings was analyzed by EDS (see Table 2). For SP coating it was possible to determine the proportion of atoms of zinc and oxygen, which revealed the oxygen deficiency expected for these films [15]. For DC coating it was not possible to determine this proportion accurately because of the interference of silicon and calcium from the substrate and the small portion of zinc atoms, about 5%. This fact is associated with the smaller thickness of the DC coating.

Table 1. Composition of the nanolayers by EDS

	DP Atom (%)	SP Atom (%)
O	66.4	47.9
Zn	8.7	52.1
Si	21.8	--
Ca	3.1	--

The absorbance spectrum was measured in both films and is presented in Fig. 3. The SP film has a higher absorption at UV region because it is thicker [14]. Also, the thickness and refractive index for both coatings were retrieved from the transmittance spectrum. After some iterative steps, it was determined that oscillations presented in Fig. 3 are consistent with a thickness of 500 ± 50 nm and a refractive index of 1.7±0.1 for SP coating; and for DC coating it corresponds 130 ± 10 nm and 1.7±0.1, respectively. By applying well known Tauc's plot method to absorbance spectrum, the energy bandgap obtained for both films was about 3.25 ± 0.02 eV, this is a value expected for pure ZnO [5, 8].

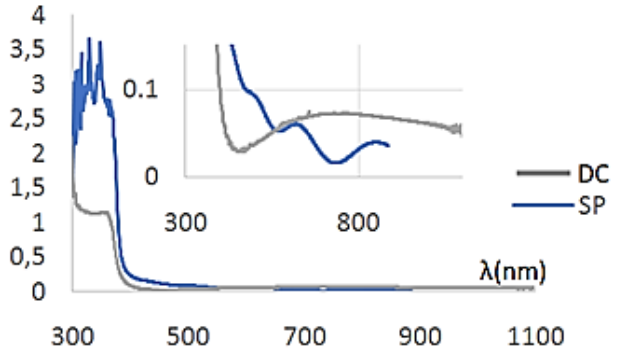

Fig. 3. Absorbance spectra measured for DC and SP coatings

XRD technique was carried out in the range of 2θ between 30º and 37º, and the results are presented in Fig. 4. It can be seen that crystallites in the sample made by SP are highly oriented in the [002] direction. In contrast to the sample made by DC, it was not observed a preferred orientation. The peaks of this pattern have relative intensities similar to that expected for commercial ZnO powder (101 > 100 > 002), shown in Fig. 4(b). This is expected because nanograins observed by AFM in DC coating (Fig. 2 (a)) do not have any preferred orientation. This difference between the patterns of SP and DC coatings were separately published by other authors [3,14,16]. Also, the peak corresponding to the 002 planes has narrower FWHM in SP coating than in DC coating, which indicates larger crystallites.

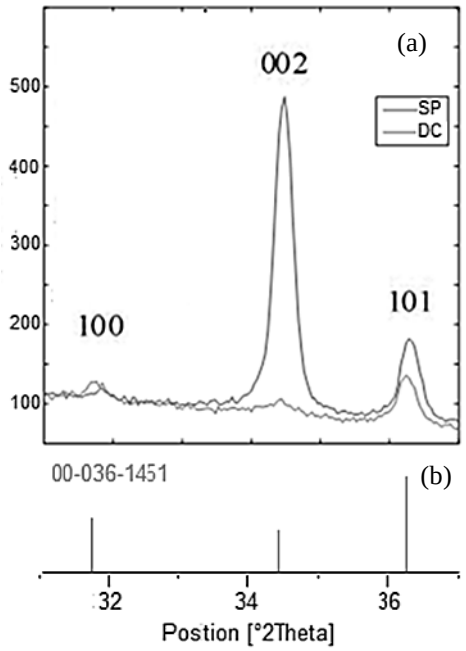

Fig. 4. (a) XRD patterns of Zinc Oxide coatings (b)XRD pattern of commercial ZnO [3]

The electrical resistance was measured for both samples and different electrode separation. The result is presented in Fig. 5. From these measurements and thickness estimated from the transmittance curve, the resistivity was estimated to be about 500 Ωcm for DC coating and 10 Ωcm for SP coating. This difference can be associated with the different thickness of DC and SP coating [11] and their microstructure, shown in Fig. 2 [5, 11].

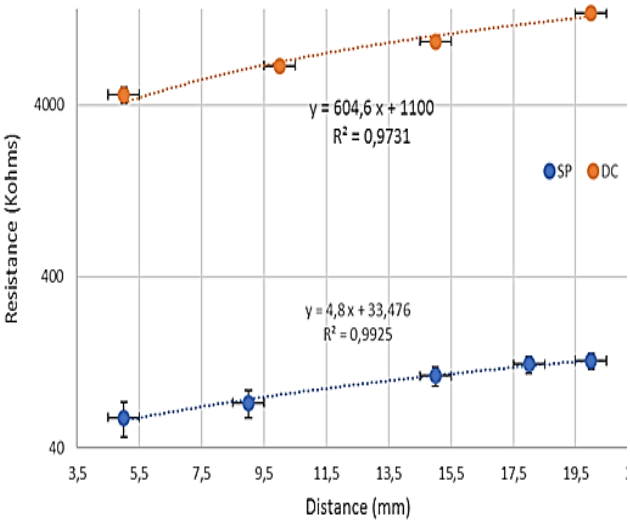

Fig. 5. The electrical resistance of the films as a function of distance for electrodes of 2.5 cm width. In the cases that error bars are not presented, the uncertainty is smaller than markers

As mentioned before, to test manufactured coatings for optical waveguiding, the well-known end-fire coupling method was employed. It was not possible to couple light into the DC film because of its reduced thickness (about 130 nm). On the other hand, a green laser was successfully coupled within the SP film. Figs. 6(a) and 6(b) show SEM images of polished end-face of SP coating and the near field intensity of guided modes, respectively.

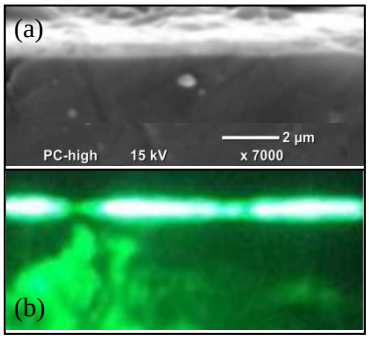

Fig. 6. (a) SEM image for end face and (b) near field of guided intensity

4. Conclusions

ZnO films were manufactured by dip-coating and spray-pyrolysis and relevant physical properties for optoelectronic applications were presented. As a relevant result, SP coating had a wider thickness (of about 500 nm) and preferred crystalline orientation in [002] direction, while the DC coating did not have any preferred crystalline orientation. The greater thickness of the SP coating made it possible to launch a green laser and the near field of guided intensity is reported. However, roughness observed in SP coating was larger than those in DC coating, which may lead to increased optical losses by scattering. Then, DC coating could be useful to manufacture low-roughness coatings for photonic applications. In order to combine the thickness of sprayed films, with the low surface roughness of dip-coated ones, it is suggested to prepare an SP coating of about 500 nm, which should be subsequently coated with a second ZnO film by dip-coating. This strategy is expected to combine the benefits of both techniques leading to a superior optoelectronic performance

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