International Congress of Science and Technology of Metallurgy and Materials, SAM - CONAMET 2013

Photoconductivity Measurements in Nanostructured ZnO and ZnO:Al Films

Claudia D. Bojorge[a], Mario F. Bianchetti[b], Horacio R. Cánepa[b], Noemí Walsöe de Reca[a,b], *†

[a]UNIDEF (MINDEF-CONICET)-CITEDEF, Juan Bautista de La Salle 4397, CP 1603 Villa Martelli, Buenos Aires, Argentina.
[b]CONICET, Juan Bautista de La Salle 4397, CP 1603 Villa Martelli, Buenos Aires, Argentina.

Abstract

ZnO is a versatile material used in numerous applications, such as antireflective coatings, transparent electrodes for solar cells, gas sensors, varistors and electro and photoluminescent devices. One of the most important properties of ZnO is the photoconductivity in the UV, due to the band-gap energy.
In this work, nanostructured pure and aluminium doped ZnO films were grown by sol-gel method. The precursor solutions were deposited with a different quantity of layers by spin-coating technique on SiO_2 substrates.
The films were characterized by X-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM). Photoconductivity study of prepared films showed that layers also exhibit sensitivity in the visible spectrum besides a remarkable and usual sensitivity to UV. Performance of pure and doped ZnO films was compared. The UV sensitivity related to the film thickness was also studied.

Keywords: ZnO, nanostructured films, photoconductivity, UV, Visible;

* Corresponding author. Tel.: +54-11-4709 8100 ext 1212; fax: +54-11-47098158
  E-mail address: cbojorge@citedef.gob.ar
* Corresponding author. Tel.: +0-000-000-0000 ; fax: +0-000-000-0000 .
  E-mail address: author@institute.xxx

1. Introduction

During the last decades, semiconductors II-VI compound have attracted the attention in the research field of semiconductor materials. One of the materials that have received a greater effort in research has been, probably, the ZnO. Its wurtzite crystal structure confers piezoelectric properties, emerging new applications, different to other compounds of the family II-VI semiconductors.

Because ZnO have a direct energy band gap about 3.3 eV and high light emission quantum efficiency, nowadays one of the main applications of these materials is the fabrication of optoelectronic devices, both light emitting diodes (Light Emitting diodes, LED) and laser diodes (Laser diodes, LD). The advantages related to a large band gap include high breakdown voltages, ability to withstand high electrical fields, reduced electronic noise and high temperatures and operating powers [Morkoç and Özgür (2009)]. In addition, the nanocrystalline ZnO is potentially promising in its applications for gas sensing [Erol et al. (2010), Fine et al. (2010)].

In this work, pure and Al doped ZnO (Zn / Al = 5%) thin films were obtained by sol-gel method. In both cases, we studied the photoconductive properties of the films with different wavelengths in the visible and UV. Furthermore, UV sensitivity was studied in relation to the thickness of the films.

2. Experimental Procedure

Clear and stable ZnO and ZnO:Al solutions were prepared using zinc acetate as a precursor salt, ethanol as a solvent and acetic acid (HAC) in aqueous solution to promote hydrolysis [Bojorge et al. (2007)]. Although this salt has limited solubility in ethanol, addition of HAC and heat from a thermostatic bath can help to complete dissolution and the formation of a stable sol.

To dope the solution with Al^{3+}, nonahydrate aluminum nitrate $Al(NO_3)_3$ $9H2O$ was added using a molar ratio Al^{3+} / Zn^{2+} equal to 5%.

The solution was deposited upon the substrate by spin-coating and dried at 200 °C during 10 min. Films were prepared with 2, 4, 6, 8 and 12 layers. All films received a final heat treatment (TT) at 450 °C during 3 h, necessary for removing carbonaceous residues and the crystallization of ZnO.

The characterization by X-ray diffraction (GIXRD) was curry out using the glancing incidence configuration and setting an incidence angle = 1°, with a conventional Philips PW 3710 (CuKα radiation). In the case of thicker films, wherein Bragg Brentano configuration could be performed, the average diameters of the crystallites of ZnO were estimated applying the Scherrer equation [Klug and Alexander, (1974)].

The general appearance of the films was studied by atomic force microscopy (AFM) and scanning electron microscopy (FESEM). This last technique also allowed study the films thickness through profile pictures.

Electrical Characterization: The electrical characterization of the films was performed by measuring the resistivity by the four-point method, using the configuration shown in Figure 1. Au contacts were deposited on the films by sputtering using a matrix, specially designed in our laboratory (Figure 2). In turn, Ag drop of paint was deposited on Au in connection places, to ensure good ohmic contacts and to protect the Au deposits onto the films.

Au electrodes are aligned and equidistantly separated, according to the matrix, by a distance $s \gg t$, where s = 3.5 mm and t is the sample thickness.
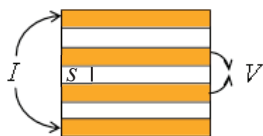

Fig. 1: Four contacts set up

Fig. 2: Matrix designed for Au contact deposition

Sample resistivity is determined injecting a current (I) between the outer electrodes and measuring the voltage (V) between the internal ones (see Figure 1). A Keithley 220 current source and a Keithley 6517B electrometer were used for inserting I and measure V, respectively. Currents between 6.10 and 9.10 Amp were used, while the input voltage limits ranged between 5 and 70 Volts.

Figure 3 shows a film and the contacts used with four points configuration.
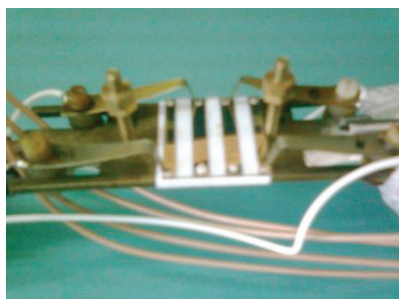

Fig. 3: Experimental metal contacts

The system was designed to be inserted into a tubular furnace, closed and at 50 °C, in order to: 1) avoid room temperature fluctuations during the measurements, to which purpose was chosen such slightly higher value that can be controlled just by heating, 2) keep the film in total darkness and isolated from any external light excitation source, 3) reduce the humidity so as not to mask the resistivity measurements, for which the furnace environment is controlled.

The sample was mounted on a support, also designed in our laboratory, with electrodes for the I feeding and the V measuring. Once assembled and placed the sample in dark oven at 50 °C, it was fed with I and determined the dark conductivity after reaching stability.

For photoconductivity measurements seven light sources with LEDs were built, each one with a specific wavelength λ (395 nm (UV), 465 nm (blue), 505 (cyan), 522.5 nm (green), 591 nm (yellow), 605 nm (amber) 625 nm (red) and 940 nm (IR). At a given position on top of the sample, it is mounted a light source that allows illuminate the film area between the inner Au contacts (Figure 4).
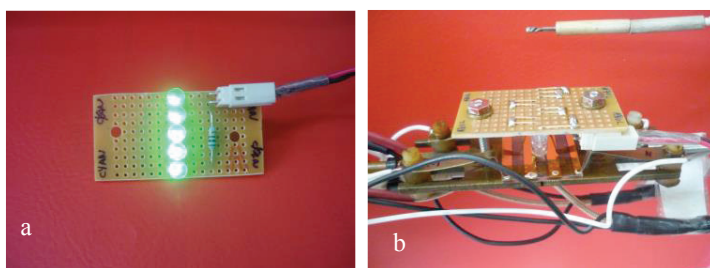

Fig. 4: a) Plaquet with LED source, b) Sample and LED source arrangement in the holder for photoconductivity measurement

After dark conductivity measurement, we proceeded to study the photoconductivity illuminating with the preassembled LEDS source. A 10 mA source stream was used. All measurements with different wavelengths were made with previous stabilization of the dark resistance, so as to always allow the system to reach steady state. This was done in order to ensure that all data have the same initial conditions. In all cases it was waited the enough time to stabilize the measurement.

3. Results

In Figure 5 and Figure 6, it can be observed GIXRD diffractogram corresponding to films with different numbers of layers, both pure and doped ZnO, 2θ ranging between 30 and 38°, which shows main peaks corresponding to the (100), (002) and (101) ZnO reflections planes.
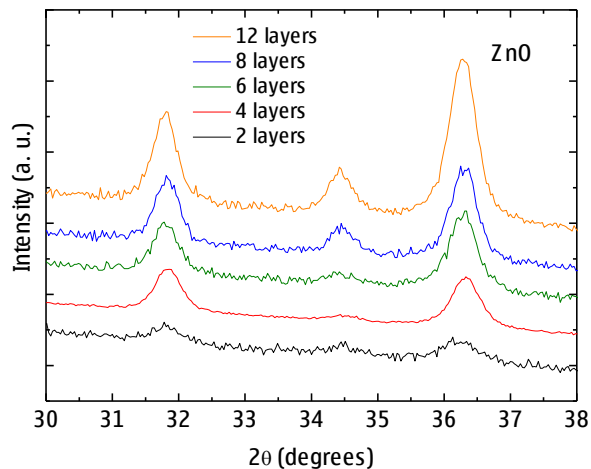

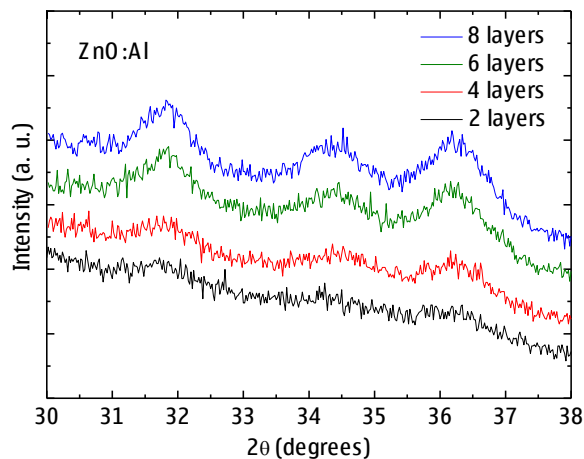Fig. 5: Diffractograms of pure ZnO samples with different numbers of layers.

Fig. 6: Diffractograms of doped ZnO samples with different numbers of layers.

Average crystallite size was estimated using Scherrer's formula, from peak broadening of the XRD spectrum, considering the width at half the height of the major peaks. In Table 4.1 appears the average of their diameters.

In both sets of films, crystallites size keeps unchanged, regardless the number of layers. In doped films, there was a significant crystallite size reduction respect to the pure ZnO case.

Table 1. Average crystallite diameter (*D*) calculated from the Scherrer equation

Sample	# layers	*D* (nm)
ZnO	6	27.1
ZnO	8	30.1
ZnO	12	28.8
ZnO:Al	4	6.6
ZnO:Al	6	6.3
ZnO:Al	8	6.1

Figure 7 a-b shows ZnO:Al film cross sections, from which it is possible to determine the thickness. Similar images were obtained for other films, which confirmed a thickness of about 18nm and 20nm per layer for the ZnO and ZnO: Al, respectively.
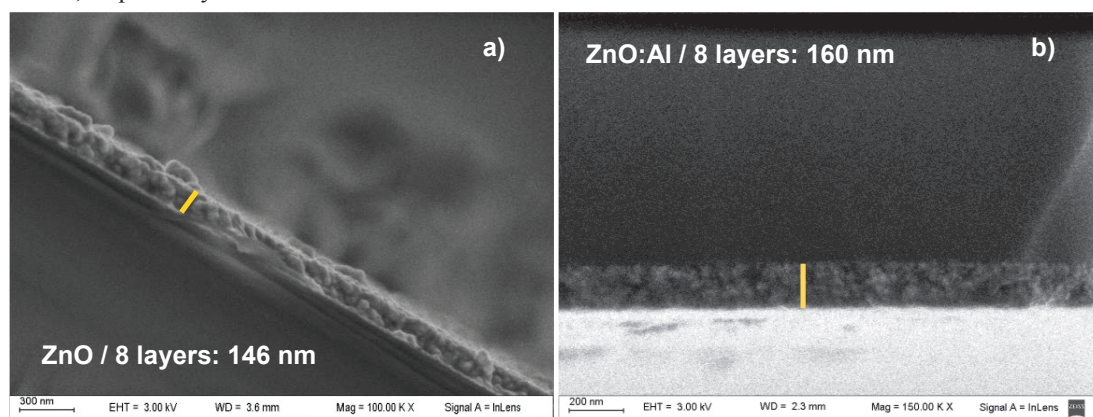

Fig. 7 a-b: FESEM micrographs of cross sections of films: a) ZnO b) ZnO: Al

In a previous work [Bojorge et al. (2012)] it was observed that the conductivity in pure ZnO films was sensitive to both visible and UV light. In this paper, we studied the photoconductivity in films of pure and Al^{+3} doped ZnO.
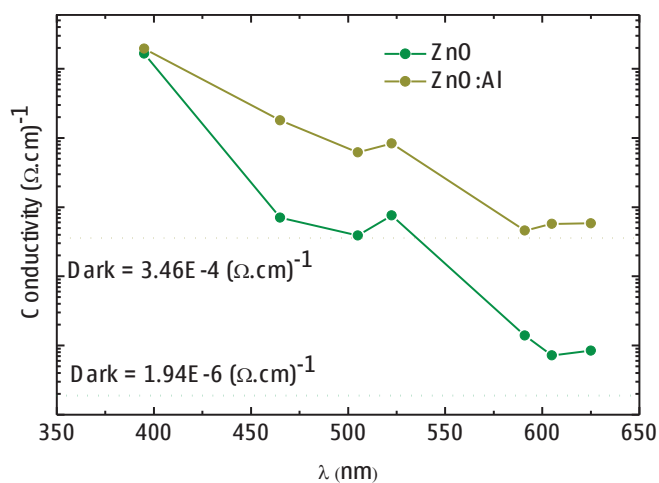

Fig. 8: 8 layer films conductivity of pure and doped ZnO, λ depending

   Figure 8 shows the variation of conductivity with the incident wavelength(λ), in a sample of 8 layers of pure and doped ZnO. It is observed that sensitive from the dark to lighted condition, is markedly greater for pure ZnO film.
   It can also be seen that, in the green spectrum range, there is an increase in conductivity, both for the pure as for the doped film. This is probably associated with the incident light of lower energy than the band gap, which excites photocarriers in deep levels to the conduction band [Basak et al. (2003), Kavak et al. (2009),Yang et al. (2002)].
   The conductivity was measured in the dark and with UV light, versus the number of layers, in pure and doped ZnO films, in order to study the UV sensitivity versus the thickness in both conditions (Figure 9). Contrary to the claims of some authors [Kavak et al. (2009), Mridha and Basak (2006)], the results in this figure show no significant changes of conductivity with the thickness. Values do not indicate the existence of a critical thickness. However, the dependence of the photoresponse properties of the ZnO thin films with the thickness has not been reported in detail [Mridha and Basak (2006)].
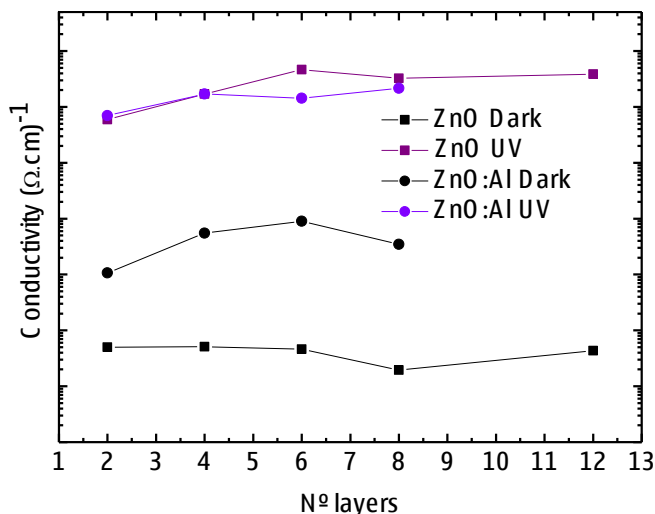

Fig. 9: Conductivity under UV illumination and in darkness, in pure and doped ZnO films with different numbers of layers.

4. Conclusions

   We obtained very good crystalline quality films with and appropriate morphology, transparent in the visible range.
   Photoconductivity measurements were performed with visible and UV wavelengths. Although the main variation of the electrical signal occurs for UV wavelength, there is considerable variation in visible light on both pure ZnO as doped films. In the IR region, photoconductive response was not observed at all. In both cases, pure and doped, an effect of increasing conductivity in the green appears(probably associated with well known green photolumiscence). It is also observed that variation of the conductivity with incident wavelength from the dark condition is markedly greater for pure ZnO films than Al^{+3} doped.
   The results of the conductivity variation as a function of number of layers, from the dark to the UV radiation condition, show virtually no major changes with thickness, contrary to some authors argue. Accordingly, the values do not indicate the existence of a critical thickness.

References

Basak, D., Amin, G., Mallik, B., Paul, G., Sen, S., 2003. Photoconductive UV detectors on sol-gel synthesized ZnO films. Journal of Crystal Growth 256, 73-77.

Bojorge, C., Bianchetti, M., Gómez, N., Walsöe de Reca, N., Cánepa, H., 2012. Nanocrystalline ZnO photoconductivity measurements. Procedia Materials Science 1, 614-619.

Bojorge, C., Cánepa, H., Gilabert, U., Silva, D., Dalchiele, E., Marotti, R., 2007. Synthesis and Optical Characterization of ZnO and ZnO:Al Nanocrystalline Films obtained by the Sol-Gel Dip-Coating Process. Journal of Materials Science: Materials in Electronics 18, 1119-1125.

Erol, A., Okur, S., Comba, B., Mermer, O., Arıkan, M., 2010. Humidity sensing properties of ZnO nanoparticles synthesized by sol–gel process. Sensors and Actuators B 145, 174–180.

Fine, G., Cavanagh, L., Afonja, A., Binions, R., 2010. Metal Oxide Semi-Conductor Gas Sensor in Environmental Monitoring. Sensors 10, 5469-5502.

Kavak, H., Senadim Tuzemen, E., Ozbayraktar, L., Esen, R., 2009. Optical and photoconductivity properties of ZnO thin films grown by pulsed filtered cathodic vacuum arc deposition. Vacuum 83, 540-543.

Klug, H., Alexander, L., 1974. X-ray Diffraction Procedures for Polycrystalline and Amorphous Materials. (Ed.). John Wiley & Sons, New York.

Morkoç, H., Özgür, Ü., 2009. Zinc Oxide: Fundamentals, Materials and Devices Technology. (Ed.). WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim.

Mridha, S., Basak, D., 2006. Thickness dependent photoconducting properties of ZnO films. Chemical Physics Letters 427, 62-66.

Yang, P., Yan, H., Mao, S., Russo, R., Johnson, J., Saykally, R., Morris, N., Pham, J., He, R. and Choi H., 2002. Controlled Growth of ZnO Nanowires and their Optical Properties. Advances Funcional Materials 12, 323-331.