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Sensing properties of ZnO Nanostructured Layers

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1. Abstract

Nanostructured ZnO layers have been deposited onto SiO_2/Si substrates by spray pyrolysis, with previously patterned interdigitated gold electrodes. We have then measured the capacitive and resistive response against ambient parameters such as relative humidity and illumination.

2. Introduction

Despite the scientific research on ZnO properties started some decades ago, nowadays it has emerged a renewed interest. Thus, during last years, ZnO has revealed as a material with a huge number of interesting physical properties which can be used in potential applications for sensing and detecting devices. In this sense, it is worth highlighting its piezoelectric properties due to its tetrahedral structure [1], its properties as humidity sensor [2], [3], its wide band gap (3.3 eV) that makes this material very interesting for UV emitting and detecting devices [4], or its high exciton binding energy (60 meV) which can yield to the development of emitting devices based on exciton recombination with high efficiencies even at room temperature [5].

Growth techniques for ZnO layers have been widely studied. Among them, we can find CVD, from which polycrystalline layers are obtained, or more sophisticated techniques such as MBE, PLD or MOCVD, from which high quality ZnO layers can be grown [5], [6]. However, in order to develop optoelectronic devices based on ZnO and its possible production at an industrial level, it's highly recommended to have cheap, fast and at low temperatures growth processes, which allow the deposition of thin films with the required characteristics for this purpose. In this sense, s*pray pyrolysis* is an optimal candidate [7]–[9].

In this work we have designed and developed a spray pyrolysis for growing ZnO layers. Prior to deposition, SiO_2/Si substrates with gold comb-shape electrodes have been designed and manufactured to be used in the devices. The electronic characterization of the devices has been carried out by using a climactic chamber to control the environmental parameters. Thus, we have determined the capacitive and resistive responses to the relative humidity and light intensity by changing both parameters. Experimental results show not only the hygroscopic properties of the ZnO but also its photoconductivity and its photodielectric properties.

3. Experimental procedure

In the following paragraphs we will describe both the developed deposition system and the design of the proposed devices.

a) Deposition system

For this work, a pyrolysis spray system was developed (Fig. 1), in order to control the different parameters involved in the growth process. In this sense, the flow control of the precursor is performed by a syringe pump with a stepper motor. The flow of the compressed inert gas used for vaporizing the precursor was controlled by a pressure regulator. The temperature of the substrate was regulated with a control system, based on a Eurotherm equipment, including a steel heater with two pairs of thermoresistances and the respective reference thermocouples.

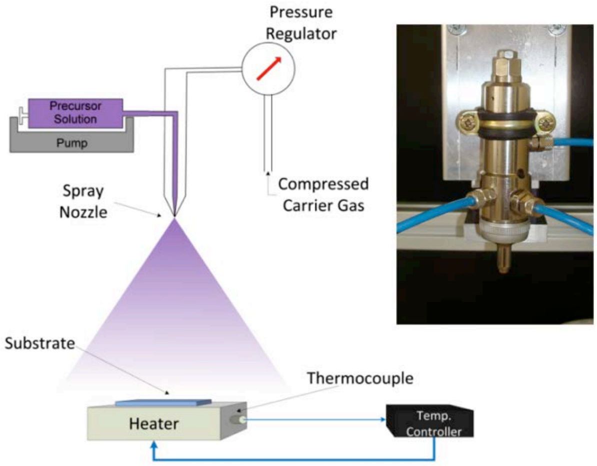

Fig.1. Scheme of the deposition system with detail.

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Parameter	*Value*
Carrier gas	N_2 (0.5 bar)
Carrier gas flux	3 ℓ/min
Solid precursor	Zn acetate di-hydrate
Solvent	Methanol
Molarity	0.5 M
Solution flux	0.5 mℓ/min
Substrate temperature	450°C
Spray time	20 min

Table 1. Deposition parameters

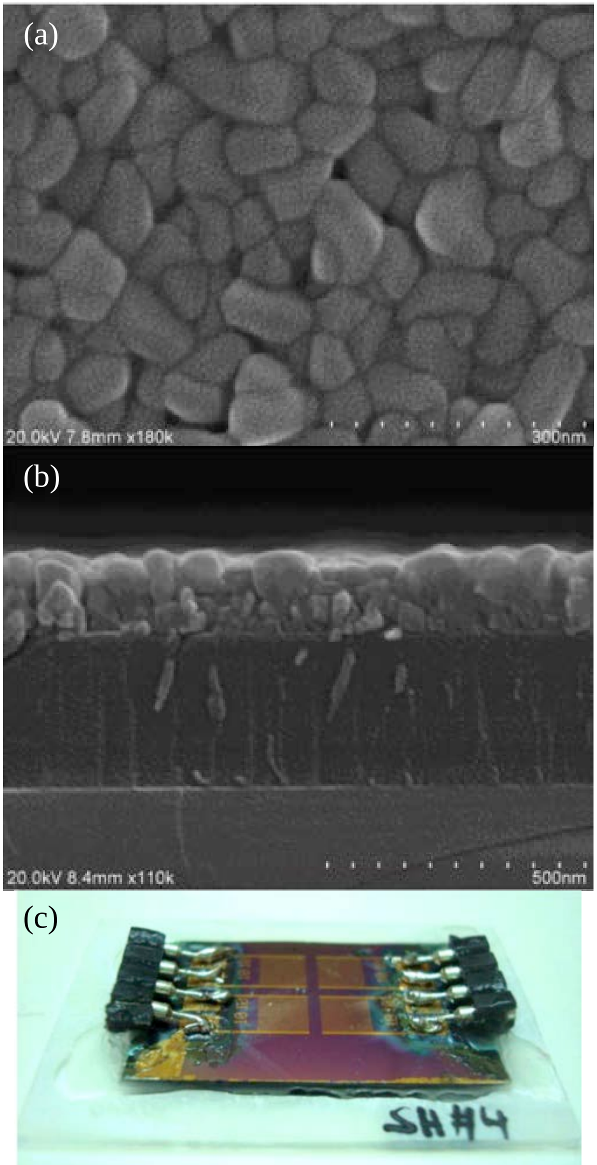

Fig.2. (a) micrograph showing the morphology of the obtained ZnO layers; (b) cross-section of the deposited structures; (c) general view of the finalized device

b) Devices design

From previous self-experience [10], we designed specific devices for characterizing the deposited layers. For this purpose, gold inter-digitated electrodes (10 µm of finger separation and 4×4 mm^2 of active area) were deposited onto 100 mm diameter SiO_2/Si wafers. Such setup will allow to easily carry out both resistance and capacitance characterizations. From the considered wafer, 2×1 cm^2 elements were carefully diced and used as substrates for the ZnO deposition. Onto such engineered substrates, ZnO was deposited with the help of mechanical masks. After some optimization steps, the considered deposition parameters are those detailed in Tab. I. Finally, connectors were directly soldered. The resulting devices as well as the morphology of the deposited layers are shown in Fig. 2. We should highlight that the relatively low deposition temperature should allow the compatibility of this deposition process with other substrates and electrodes materials. As observed, nanostructures (30-50 nm size) are arranged forming a layer of about 100 nm thickness homogeneously onto the useful area of the devices.

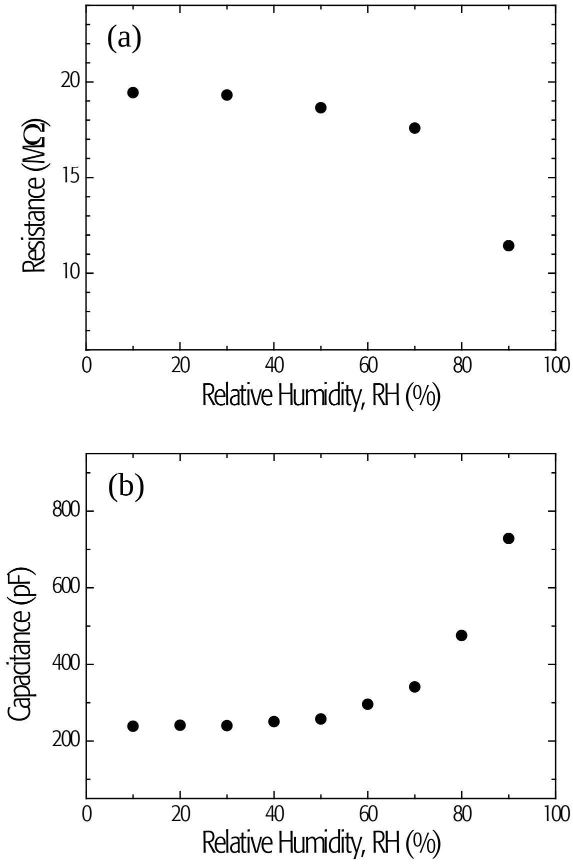

Fig. 3. Response to relative humidity, experimental results: (a) Resistance; (b) Capacitance

4. Experimental results

As a preliminary step, before performing the measurements, the considered devices were conveniently aged in a controlled high relative humidity atmosphere (95%) for 24 hours at room temperature (25 degrees Celsius).

a) Relative humidity

We used an automated climatic chamber (Challenge 600) for characterizing the electrical properties of the obtained devices as a function of the relative humidity (RH). The resistance and the capacitance were measured for a constant temperature (25ºC) and under darkness conditions for avoiding crossed effects. We used AC polarization for avoiding over-charging issues in the deposited layers. Obtained results are shown in Fig. 3. As can be observed, the value of the resistance lowers with RH and the value of the capacitance increases with RH. It is worthy to note that the sensitivity is higher for higher RH conditions.

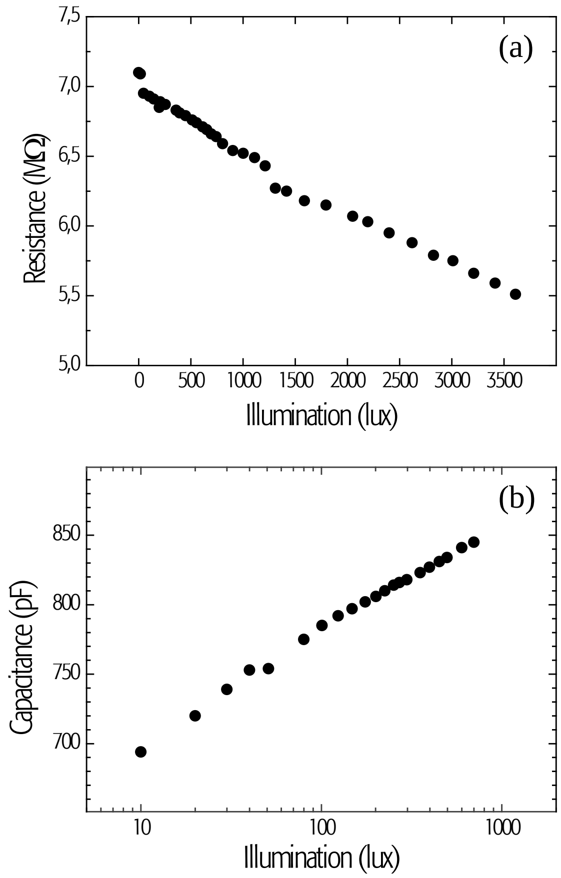

Fig. 3. Response to light intensity, experimental results: (a) Resistance; (b) Capacitance

a) Light intensity

For constant ambient parameters (RT= 25°C; RH= 50%), we measured the dependence of the electrical parameters with the light intensity. We used an array of white LEDs with controlled intensity. The obtained experimental results are shown in Fig. 4. We can observe a linear response with illumination of the resistance, while the capacitance has a logarithmic dependence. The resistance decreases due to the photoconductivity of the ZnO, and the capacitance rises, showing the photodielectric properties of the material.

5. Conclusions

Spray pyrolysis, while maintaining its intrinsic advantages of low cost, low temperature and moderate deposition speed, has proved its utility to produce nanostructured layers with enough quality to be used for sensing purposes. So obtained layers can be used in ambient parameters sensing such as light intensity and relative humidity. Moreover, a rapid calibration of the devices could be done due to the linear response of the electric parameters to the light intensity.

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References

[1] A. Dal Corso, M. Posternak, R. Resta, and A. Baldereschi, “Ab initio study of piezoelectricity and spontaneous polarization in ZnO,” *Phys. Rev. B*, vol. 50, no. 15, pp. 10715–10721, Oct. 1994.

[2] Q. Qi, T. Zhang, S. Wang, and X. Zheng, “Humidity sensing properties of KCl-doped ZnO nanofibers with super-rapid response and recovery,” *Sensors Actuators B Chem.*, vol. 137, no. 2, pp. 649–655, 2009.

[3] L. Chen and J. Zhang, “Capacitive humidity sensors based on the dielectrophoretically manipulated ZnO nanorods,” *Sensors Actuators A Phys.*, vol. 178, pp. 88–93, 2012.

[4] C. Soci, A. Zhang, B. Xiang, S. A. Dayeh, D. P. R. Aplin, J. Park, X. Y. Bao, and Y. H. Lo, and D. Wang, “ZnO Nanowire UV Photodetectors with High Internal Gain,” 2007.

[5] Ü. Özgür, Y. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Doğan, V. Avrutin, S.-J. Cho, and H. Morkoç, “A comprehensive review of ZnO materials and devices,” *J. Appl. Phys.*, vol. 98, no.

4, p. 041301, Aug. 2005.

[6] Z. L. Wang, “Zinc oxide nanostructures: growth, properties and applications,” *J. Phys. Condens. Matter*, vol. 16, no. 25, pp. R829–R858, Jun. 2004.

[7] P. S. Patil, “Versatility of chemical spray pyrolysis technique,” *Mater. Chem. Phys.*, vol. 59, no. 3, pp. 185–198, 1999.

[8] D. Perednis and L. J. Gauckler, “Thin Film Deposition Using Spray Pyrolysis,” *J. Electroceramics*, vol. 14, no. 2, pp. 103–111, Mar. 2005.

[9] R. Ayouchi, F. Martin, D. Leinen, and J. . Ramos-Barrado, “Growth of pure ZnO thin films prepared by chemical spray pyrolysis on silicon,” *J. Cryst. Growth*, vol. 247, no. 3, pp. 497–504, 2003.

[10] S. Rajappan-Achary, S. Agouram, C. Reig, J. F. Sánchez-Royo, M. C. Martínez-Tomás, and V. Muñoz-Sanjosé, “Self-Assembled Zinc Oxide Quantum Dots Using Spray Pyrolysis Methodology,” *Cryst. Growth Des.*, vol. 11, no. 9, pp. 3790–3801, Sep. 2011.