Zinc Oxide Nanostructures:New Properties for Advanced Applications

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***Abstract* – Zinc oxide is a material which exhibits a variety of new properties at nanometer dimensions. Various synthesis techniques have been carried out to provide growth of nanowires, nanorods, nanorings, nanosprings, and nanobelts of ZnO under various conditions. These nanostructures show that ZnO possesses probably the richest family of nanoarchitectures among all materials, including their structures and properties. Such nanoarchitectures are potential building blocks for novel applications in optoelectronics, sensors, photovoltaic and nano-biomedical sciences. This work presents a review of various nano architectures of ZnO grown by the electrochemical, hydrothermal and solid–vapor phase techniques and their properties. The possible applications of ZnO nanowires as sensors, nano-DSSC, photodetectors and nano-LEDs will be presented.**

***Index Terms* – ZnO, nanowire, nanorod, nanosensor, nano-LED, nanophotodetector.**

I. INTRODUCTION

Low-dimensional ZnO materials have become the focus of a lot of researches due to their performances in electronics, optoelectronics, photonics and biomedical applications. In the last decade, the growth of ZnO has been an active research field due to their applications as sensors and catalysts. However, since the nanotechnology initiative led by the USA, investigations of one-dimensional (1D) materials, like nanowires and nanorods has become a leading edge for the nanotechnologies and for nanoscience. The reduction of material size induces new electrical, chemical, optical and mechanical performances, which are believed to be the results of aspect-ratio impact, size and quantum confinement effects. 1D nanorods are ideal for investigating the transport process in confined spaces. This can result in future understanding of new phenomena in low-dimensional structures. It could be a forward step for developing new generation of nanodevices with better performance [1-8].

In this context zinc oxide is one of the key materials. It combines strong piezoelectric and pyroelectric properties. Also, ZnO posses a wide direct band-gap (3.36 eV), which is good for optoelectronic applications. The exciton binding energy (60 meV) in ZnO crystal is higher that in GaN, which can give excitonic emission at room temperature more efficient than other materials. At the same time, ZnO is a transparent material to visible light and could be doped easily to obtain lower resistivity and/or bandgap for specific applications. It is a strong candidate for high temperature electronic devices that can reliably operate in space and other harsh environments [3].

The topic of our presentation here is to review the low-dimensional structures that have been grown for ZnO by electrochemical or hydrothermal deposition and corresponding mechanisms. The potential applications of ZnO low-dimensional structures in novel nanodevices will be discussed.

II. EXPERIMENTAL

The fabrication method of nanosensors by using individual ZnO nanowire or nanorod released from an agglomeration of nanowires as-grown on initial substrate has been described in our previous works [5,6] and reviewed in [3,4]. Nanowires can be released from the initial substrate by sonication in ethanol or it can be used a direct contact technique can be used to transfer nanowires to a SiO_2-coated Si substrate. These procedures can be found in our previous works [4,5]. Rigid contacts were fabricated with a single ZnO nanowire on the sensor substrate template (glass with Cr/Au as electrodes) by using FIB metal deposition. For the sensor characterization, the measuring apparatus consists of a closed quartz chamber connected to a gas flow system [4-6]. The concentration of gases for test was measured using a pre-calibrated mass flow controller. Gases and air were introduced to a gas mixer via a two-way valve using separate mass flow controllers. By monitoring the output voltage across the nanorod based sensor, the resistance was measured in dry air and in a test gas. A computer with suitable LabView interface allows all controls and acquisition of data. A linear behavior of the current-voltage curves was recorded, which is important for the sensing. ZnO nanowires have also been synthesized by electrodeposition, a soft deposition technique that is suitable with plastic lightweight substrates [7].

III. RESULTS

A scanning electron microscope image of the connected ZnO nanowire is presented in Figure 1. Focused ion beam (FIB) instrument was used to pattern metal electrodes contacting both ends of a single ZnO nanowire. The separation of the electrodes was about 5 μm. The fabricated device based on a single wire of 100 nm in diameter shown in Figure 1a, was used in our studies.

Figure 1b shows the transient response of the 100 nm ZnO-nanowire gas sensor under exposure to 100 ppm of H_2 gas at room temperature.

Ultraviolet (UV) photoconductive nanosensors based on an individual ZnO nanowire (100 nm in diameter) are important for nanoscience. This nano-detector is prepared in a FIB set-up by using nanodeposition for metal electrodes and studied as was reported before [8,9]. The photoresponse of the ultraviolet sensor demonstrated that the output signal of the sensors is reproducible under UV irradiation. The photoresponse and characteristics of the ZnO nanowire device demonstrates that focused ion beam process offers a way to fabricate novel nanodevices on a single ZnO nanowire with diameters as small as 100 nm [6]. The response and recovery times to UV light exposure are relatively fast for a single ZnO nanowire photodetector compared to an individual zinc oxide nanorod grown by aqueous chemical deposition [9].

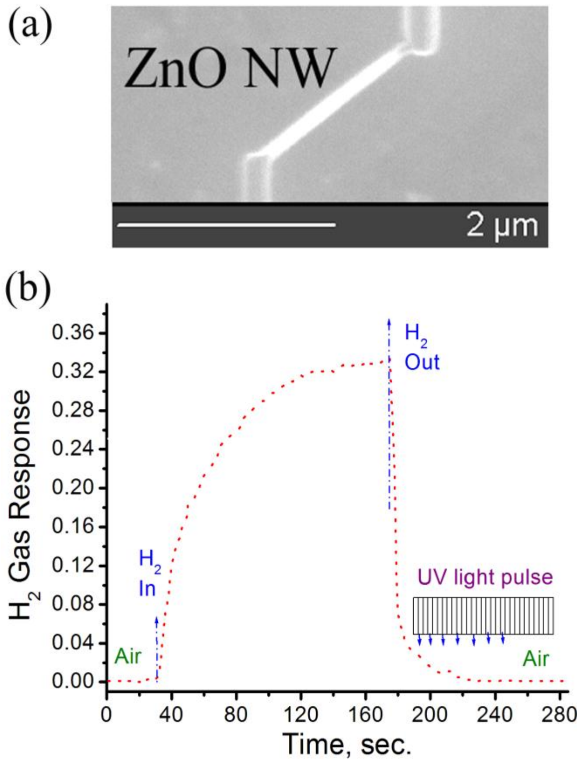

Fig. 1. (a) FESEM image of a single ZnO nanowire (NW) connected in a nanosensor structure by FIB technique. (b) Gas response curves of the 100 nm zinc oxide nanowire–based gas sensor under exposure to 100 ppm of H_2 gas at room temperature.

The epitaxial synthesis of ZnO nanowire arrays on a *p*-type GaN (0001) single crystalline thin film on sapphire by an electrochemical technique was demonstrated for the first time in our works [10,11]. The nanowires were directly epitaxially grown onto the *p*-GaN films with an in-plane relationship of ZnO[10-10] parallel to GaN[10-10]. By GA-XRD experiments, the ZnO mosaicity was shown to be as low as 1.18°. The n-ZnO NWs/*p*-GaN heterostructure was integrated in a light emitting diode structure device [10,11]. The rectifying behavior was shown with a forward current onset at 3V. The LEDs emitted a unique UV-light centered at ~393 nm for either as-prepared or annealed samples. The light emission turn-on voltage was ~4.4 V and the UV-emission was very bright even at low applied forward bias ~6.4 V. Our data clearly state the remarkable quality of the electrochemical ZnO material and ZnO-NWs/*p*-GaN interface as well as effectiveness of electrodeposited epitaxial ZnO as an active layer in UV-LED structure [10,11]. By copper-doping the ZnO NWs, we have shown that the emission wavelength of the LED structure could be shifted towards the visible wavelength region [12]. ZnO NWs were also grown by electrodeposition on *p*-Si and LED structures, were made and discussed in Ref. [13]. Other applications of electrodeposited zinc oxide low-dimensional structures also include dye-sensitized solar cells which were reported in Ref.[14]. The ZnO wires ensure a fast electron transfer from the excited dye to the back contact of the photoanode [14]. Photodetectors and other devices structures were reported in other papers [15-17]. In Appendixes A-E, some morphological and structural properties of the ZnO nanostructures and applications have been shown. More detailed description for these low-dimensional structures and their characteristics have been reported in our works [2-20].

IV. CONCLUSION

We report on zinc oxide nanostructures – properties and possible applications in future devices. It has been shown a single nanowire nanosensors made from ZnO nanowire can be produced. Fabricated nanodevices showed a promising sensitivity to H_2 gas, which makes possible its further applications in sensors. The presented single ZnO nanowire sensor proves to be promising for application in various processes [3,4]. Also, ZnO nanowires grown by electrodeposition or hydrothermal techniques have been integrated in LEDs and DSSC structures and have been discussed here.

APPENDIX A

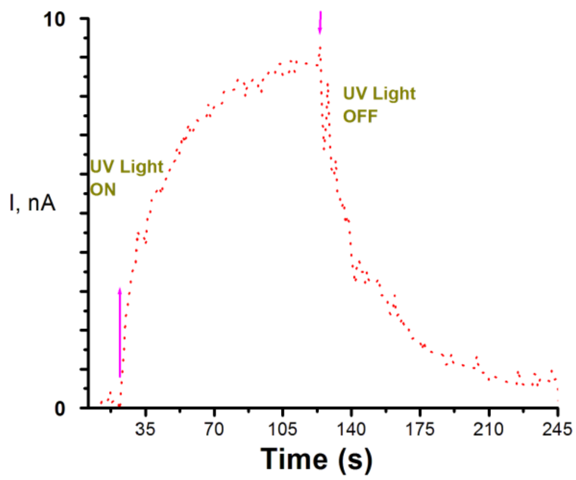

Fig. A. The UV response for a single ZnO nanowire-based UV photoconductive detector.

APPENDIX B

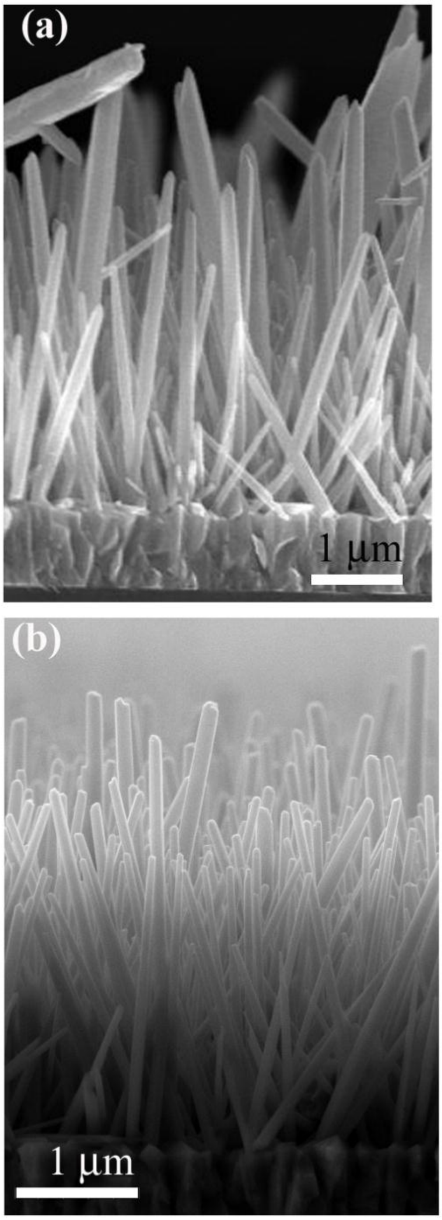

Fig. B. SEM image of the ZnO nanowires grown by an electrochemical technique at 90 °C from $ZnCl_2$ and KCl solution. (a) pure ZnO grown for 9000s; (b) Cd-ZnO grown on FTO substrate for 7200 s. These nanowires were used as building nanoblocks for LED, DSSC solar cells and for nanosensors structures.

APPENDIX C

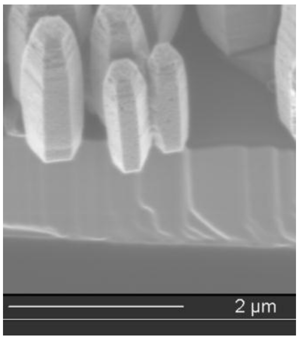

Fig. C. SEM image (tilted 65 °) of epitaxial ZnO Nanorods grown on *p*-GaN by hydrothermal technique. It is forming a heterostructure (*n*-ZnO/*p*-GaN) used for low-dimensional-LED applications.

APPENDIX D

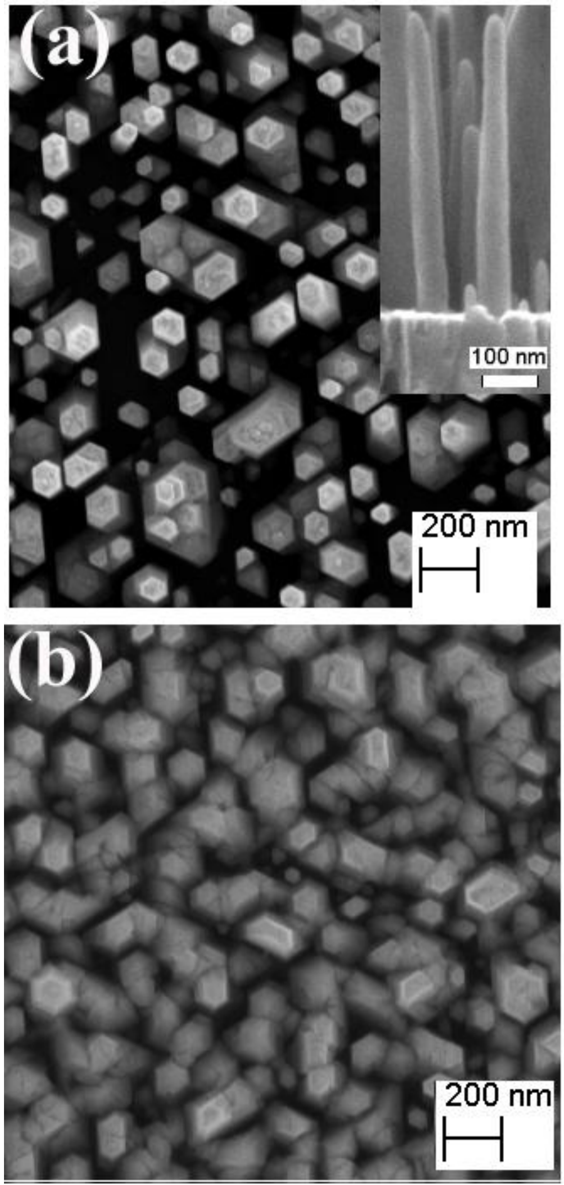

Fig. D. SEM image of epitaxial ZnO Nanowires electrodeposited on p-GaN (0.10 mM $ZnCl_2$) and (b) (0.25 mM $ZnCl_2$). Inset shows cross-sectional view of the ZnO nanowires on p-GaN single crystal forming a heterostructure used for nano-LED applications.

APPENDIX E

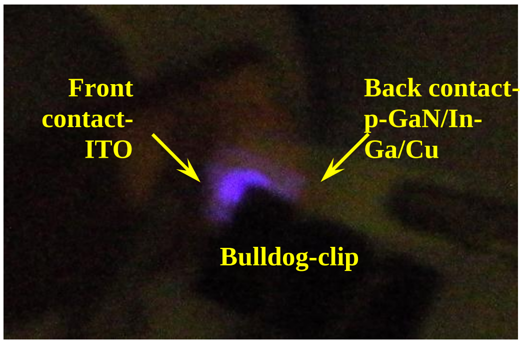

Fig. E. The inset shows an image of the blue- light emission spot under a dc bias of 8.5 V at room temperature from zinc oxide nanowires grown on *p*-GaN substrate.

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