THE EFFECT OF SURFACE FUNCTIONALIZATION AND DOPING ON NANOWIRE DEVICES PERFORMANCES

Oleg Lupan[1,2,3], Lee Chow[2], Ion Tiginyanu[1,4], Victor Şontea[1], Thierry Pauporte[3]
[1]Technical University of Moldova
[2]University of Central Florida, U.S.A.
[3]Centre National de la Recherche Scientifique, France
[4]Academy of Sciences of Moldova
lupan@mail.md

Abstract. *The paper deals with an important scientific problem of enhancement performances of nanowire-based devices. Zinc oxide nanowires and nanorods were grown by electrochemical deposition and hydrothermal techniques. X-ray diffraction, scanning electron microscopy, transmission electron microscopy, X-ray photoelectron spectroscopy, sensing characterization, photoluminescence and electroluminescence demonstrates that the obtained nanowires/nanorods represent crystalline zinc oxide. Nanowire-based nanosensors were fabricated by using FIB/SEM and it is demonstrated that the doped nanorod/nanowire-based sensors have higher sensitivity and faster response. Electroluminescence studies of nanowire-based LEDs showed that the emission wavelength of the light can be tuned.*

Keywords: *zinc oxide, nanowire, nanodevice, nanosensor, nano-LED.*

I. Introduction

Zinc oxide (ZnO) is a versatile wide band gap semiconductor and it has been extensively studied as the new material for optical-electrical and photovoltaic devices. Pure or doped ZnO nanowires have shown unique multifunctional properties promising for various applications in gas sensors [1], light emitting diodes [2], dye-solar cells [3], field-effect-transistors FET [4], etc. ZnO nanowire nanosensors are very promising to detect hydrogen at elevated temperature [5]. At elevated operating temperature, the conductivity of zinc oxide nanowires can be influenced by the ambient atmosphere. It can also be used to detect hydrogen and hydrocarbon gases at room-temperature. But at low temperature, the oxygen-vacancies diffusion is frozen and gas response is low, as well as the response/recovery time is long. The solution of these problems is surface functionalization and/or doping of zinc oxide nanowires to obtain lower operating temperature, higher gas sensitivity and faster response. Consequently, single nanorod/nanowire ZnO-sensors show changes in the conductivity under exposure to gases, which makes it highly demanded for the development of an electronic nose. Herein, we report the synthesis, microstructure, and the gas sensing characteristics of ZnO nanowires. The gas sensing shows that the ZnO multiple nanowire gas sensor and individual nanowire nanosensor have reversible response to H_2 and CH_4 gases at room-temperature. The results demonstrate the possibility to develop ZnO nanowire-based low power consumption gas nanosensors. Also, tunable-wavelength light emitting diodes based on nanowires have been demonstrated.

II. Nanotechnologies of nanowires/nanorods synthesis and nanodevice fabrication

ZnO and Ag, Cd, Cu, Al-doped ZnO nanowires and nanorods were grown by an electrochemical procedure and by hydrothermal technique discussed in details in previous reports [1,6-8]. Slices of *p*-type Si (100) were used as substrates for the synthesis of the ZnO and Cu-ZnO material

in hydrothermal process. For the electrodeposition of doped ZnO nanowire arrays, F-doped tin oxide (FTO) film supported on a glass substrate with a resistance of 10 Ω/□ [7-8]. More details can be found in our papers as reported previously [7-9]. Manipulation and reactions were carried out in air inside a fume hood.

The size and morphology of the samples with ZnO nanorods were observed with a JEOL scanning electron microscope (SEM). The compositional analysis of ZnO nanorods was carried out using Energy dispersive X-ray spectroscopy (EDX), in combination with SEM. X-ray powder diffraction (Rigaku 'DB/MAX' powder diffractometer) was used for structural analysis using Cu Kα radiation (λ = 1.54178 Å). The ex situ prepared samples were mounted on a molybdenum sample holder and subsequently transferred into an ultrahigh vacuum system (UHV) system equipped with a hemispherical electron energy analyzer (Phoibos 100, SPECS GmbH) and a dual-anode (Al K_α, 1486.6 eV and Ag Lα, 2984.4 eV) monochromatic X-ray source (XR50M, SPECS GmbH). Vibrational modes in pure and doped ZnO nanorods/nanowires were obtained from Raman backscattering experiments in a micro-Raman setup Horiba Jobin Yvon LabRam IR spectrometer. Room-temperature photoluminescence (PL) was excited by the 4th harmonic (266 nm) of an YAG:Nd laser and dispersed with a HR250 monochromator (Jobin - Yvon) coupled to an UV - enhanced Intensified Charge Coupled Device (ICCD) (Roper). The gas response was measured using a two-terminal ZnO rod device [5]. Its characteristics were measured using a semiconductor parameter analyzer with input impedance of 2.00×10^8 Ω. The fabricated device structure was put in an environmental chamber to detect different gasses (H_2, O_2, C_2H_5OH, CH_4 and natural gas-LPG). The humidity of the gas mixture was about 60 RH%. The gas flow was controlled by MKS mass flow controller and test system as reported before [5,10]. The device electroluminescence was collected by an optical fiber connected to a CCD Roper Scientific detector (cooled Pixis 100 camera) coupled with a SpectraPro 2150i monochromator. The monochromator focal lens was 150 mm, grating of 300gr/mm blazed at 500 nm in order to record the emission of the ZnO in the whole near-UV-visible range.

III. Results and discussions

Figure 1a shows a scanning electron microscopy (SEM) image of the quasi-aligned high aspect ratio Cd-doped ZnO nanowire array synthesized by electrodeposition on FTO substrate.

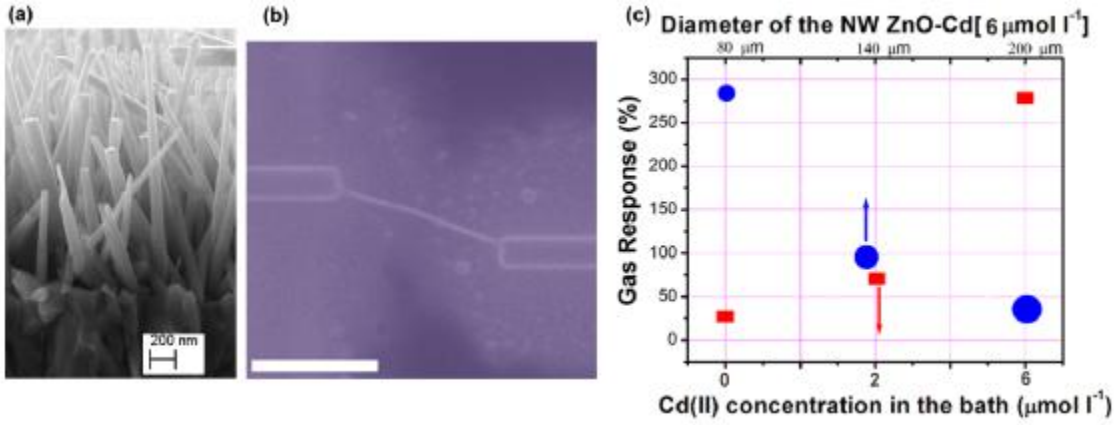

Fig.1. (a) SEM micrographs (cross-section view) of the ZnO-Cd (6 μM $CdCl_2$ in the electrolyte) nanowire layers electrodeposited on FTO substrate. (b) SEM image of the ZnO-Cd nanowire integrated in an nanosensor. Scale bar is 2 μm. (c) Gas response to 100 ppm H_2 gas pulse of a single ZnO-Cd nanowire (80 nm) versus concentration of [Cd](0-6 μM $CdCl_2$ in the electrolyte) and versus diameter (80, 140 and 200 nm).

These nanowires have uniform lengths of 2–3 μm and diameters of 50–200 nm. NWs are well facetted with hexagonal cross-sections (not shown). The aspect ratio of doped ZnO NWs is

about 30, which is 50% higher than that of pure ZnO NW under the same growth conditions [8]. XPS analysis was conducted to determine the presence of the Cd dopants and their chemical state inside the ZnO matrix. According to XPS spectra there were detected Zn-2p and Cd-3d core level regions of the Cd-doped ZnO nanowires. The Zn-2p region shows a doublet at 1021.7 eV and 1044.8 eV corresponding to the Zn-$2p_{3/2}$ and $2p_{1/2}$ core levels (not presented). The Cd-3d region also shows a doublet tentatively assigned to cationic Cd ($Cd^{\delta+}$, $3d_{5/2}$ = 405.6 eV and $3d_{3/2}$ = 412.4 eV). High-resolution TEM images taken from the edge of the sample and electron diffraction characterization indicate that the ZnO nanowire is grown along the c- axis. XRD studies of the crystal structure indicates only ZnO peaks which demonstrates that it matches the lattice spacing of crystalline zinc oxide in the wurtzite structure (space group: $P6_3mc$(186); a = 0.3249 nm, c = 0.5206 nm). A slight shift of about 0.015° or 0.023° to lower 2θ values for (002) peak for ZnO:Cd (2μM) and ZnO:Cd (6μM) compared to pure ZnO were measured by XRD.

Figure 1b shows nanosensor structure of the single-nanowire contacted by FIB. Figure 1c shows a comparison of the gas response of a pure- and a Cd-doped ZnO NW nanosensors. It clearly demonstrates the dependence of the gas response on the concentration of Cd-doping of ZnO NW-based sensors. It can be seen that by doping cadmium the sensitivity to H_2 at room-temperature operation can be improved. The Figure 1c demonstrates the dependence of the gas response on the diameter of ZnO NW-based sensors. The highest gas response (about 274%) was obtained from a sensor based on a single Cd (6 μM) - doped ZnO NW with diameter less than 100 nm. For comparison, 140 nm and 200 nm NW shows a lower gas response to H_2, less than 68% and 35%, respectively. Our results demonstrate the importance of using thinner and doped nanowires to design highly sensitive H_2 sensors, which can operate without need of elevated temperatures. Also, power consumption of a nanosensor is ~5nW, which makes it very competitive for integration in wireless nanosensors networks.

Another approach is surface functionalization to improve sensing response and to control gas response in different ambient conditions. As mentioned in our previous reports, ZnO material was dipped in a palladium chloride solution and thermal treated at 400 ^oC before in-situ lift-out fabrication process for sensor structure. Afterwards, the zinc oxide samples were first transferred onto the intermediate Si/SiO_2 substrate in order to reduce the sample density and avoid charging problems in the FIB system and fabricated a sensor structure [10]. The fabricated single ZnO wire gas sensor was put in a test chamber to detect natural gas and other gases, such as H_2, O_2, CO_2, CO and ethanol. The maximum response was obtained for natural gas in this case. The room-temperature sensitivity of the single ZnO wire sensor increases about 5% within 30 s. Afterwards, the NG gas is turned off and the detector resistance decreases back to the initial value. The temperature dependence of natural gas sensitivity of the fabricated single ZnO wire sensor structure demonstrated that different operating temperatures of ZnO sensor lead to different responses to NG with a maximum at about 400 °C. This observation could be explained by the phenomenon that at elevated operating temperature methane more easily decomposes in species, which favour increase of response value. The gas sensing mechanism can be explained by the charge transfer that takes place during adsorption/desorption of an oxygen species on surface. The sensing mechanism is based on interaction between negatively charged oxygen adsorbed on the zinc oxide surface and gas to be detected. For Cu-doped ZnO wire-based sensor it was measured the ~44% sensitivity to H_2. Quick response, faster recovery times (comparatively to pure ZnO), and selectivity were found to be significant useful for further development of H_2 sensor at room temperature.

The room-temperature electroluminescence spectra of the device structures made from $Zn_{1-x}Cd_xO$ nanowires (grown in 2 and 6 μM $CdCl_2$ in the bath) were studied and compared with those based of pure ZnO NWs/p-GaN used as reference. In each case, it was seen a single short wavelength emission shifted towards the violet range with Cd-alloying of ZnO.

IV. Conclusion

In this work, the nanoscale sensor based on a single Cd-doped ZnO nanowire was fabricated by using focused ion beam set-up. Nanosensor has been shown to have enhanced performance, e.g., high sensitivity (able to detect down to 100 ppm of H_2), good selectivity (poor response to CH_4, C_2H_5OH, CO, and ammonia), and low power consumption of <5 nW at 2 mV compatible to a portable device. The diameter dependence of the gas response of a single Cd-ZnO nanowire synthesized by electrochemical method was studied. It was shown that sensitivity depends of Cd-doping. It was demonstrated the dependence of selectivity H_2 gas. A single Pd-functionalized ZnO wire natural gas sensor structure for monitoring of natural gas was demonstrated.

V. References

1. Tiginyanu I. M., Lupan O., Ursaki V. V., Chow L., Enachi M. Nanostructures of Metal Oxides. Comprehensive Semiconductor Science & Technology, Chapter 3.11, 2011, pp. 396-479.

2. Lupan O., Pauporté Th., Viana B. Low-Voltage UV-Electroluminescence from ZnO-Nanowire Array/*p*-GaN LED, Advanced Materials. 22(30), Aug 2010, pp. 3298–3302.

3. Lupan O., Guérin V.M., Tiginyanu I.M., Ursaki V.V., Chow L., Heinrich H., Pauporté T. Well-aligned arrays of vertically oriented ZnO nanowires electrodeposited on ITO-coated glass and their integration in dye sensitized solar cells. Journal of Photochemistry and Photobiology A: Chemistry Volume 211(1), March 2010, pp. 65-73.

4. Ozgur U., Hofstetter D., Morkoc H. ZnO Devices and Applications: A Review of Current Status and Future Prospects. Proceedings of the IEEE Volume 98(7) , July 2010, pp. 1255-1268.

5. Lupan O., Emelchenko G.A., Ursaki V.V., Chai G., Redkin A.N., Gruzintsev A.N., Tiginyanu I.M., Chow L., Ono L.K., Roldan Cuenya B., Heinrich H., Yakimov E.E. Synthesis and characterization of ZnO nanowires for nanosensor applications. Materials Research Bulletin Volume 45(8), August 2010, pp. 1026-1032.

6. Lupan O., Chow L., Ono L. K., Roldan Cuenya B., Chai G., Khallaf H., Park S., Schulte A. Synthesis and Characterization of Ag- or Sb-Doped ZnO Nanorods by a Facile Hydrothermal Route. J. Phys. Chem. C Volume 114 (29), July, 2010, pp 12401–12408.

7. Lupan O., Pauporté T., Viana B., Aschehoug P. Electrodeposition of Cu-doped ZnO nanowire arrays and heterojunction formation with *p*-GaN for color tunable light emitting diode applications. Electrochimica Acta Volume 56, February 2011, pp. 10543-10549.

8. Lupan O., Pauporté Th., Le Bahers T., Ciofini I., Viana, B. High Aspect Ratio Ternary $Zn_{1-x}Cd_xO$ Nanowires by Electrodeposition for Light Emitting Diode Applications. Journal of Physical Chemistry C Volume 115(30), 2011, p. 14548-14558.

9. Lupan O., Pauporté Th., Viana B., Tiginyanu I. M., Ursaki V. V., Cortés R. Epitaxial Electrodeposition of ZnO Nanowire Arrays on p-GaN for Efficient UV-Light-Emitting Diode Fabrication. ACS Appl. Mater. Interfaces, 2010 Volume 2 (7) , July, 2010, pp. 2083–2090.

10. Lupan O., Ursaki V.V., Chai G., Chow L., Emelchenko G., Tiginyanu I.M., Gruzintsev A.N., Redkin A.N. Selective hydrogen gas nanosensor using individual ZnO nanowire with fast response at room temperature. Sensors and Actuators B: Chemical Volume 144(1), 2010, pp. 55-66.