SELECTIVE GAS SENSOR BASED ON ONE-DIMENSIONAL STRUCTURE OF ZnO NANOROD

O. Lupan[1,2], L. Chow[2], G. Chai[3]
[1]Technical University of Moldova,
[2] University of Central Florida, U.S.A.,
[3] Apollo Technologies, Inc., FL 32746, U.S.A.

INTRODUCTION

Transferable one-dimensional (1-D) ZnO nanorods grown along the *c*-axis have been synthesized by new hydrothermal route based on aqueous-solution method. X-ray diffraction (XRD), scanning electron microscopy (SEM), and micro-Raman spectroscopy show that obtained ZnO nanorods are of high crystalline nanomaterial with a wurtzite structure. Gas sensing investigations show that obtained single ZnO nanorod –based sensor posses a good selectivity and sensitivity to hydrogen gas. Pure and doped 1-D – ZnO nanorod could possibly be used as a building unit in selective gas sensor opening opportunities for the fabrication of multifunctional nanodevices.

1. ZnO - NANOROD - BASED SELECTIVE SENSORS

In present, selective sensors proposed use an indirect approach (e.g. Raman spectroscopy, gas chromatography or gas chromatography coupled to mass spectrometry (GC/MS), etc.) or requiring complicated components to detect the presence of certain gases in atmosphere. In recent years, there has been a continuous increase towards requirements to gas sensitivity/selectivity in the industry. These developments are motivated by the fact that each process has the potential of leaving residues that reduce the purity of used gases. Furthermore, contaminants may be introduced from storage or transport vessels. In the quality control of gases, the methods generally used are analytical techniques such as gas chromatography or GC/MS [1]. These techniques are very sensitive/selective and at the same time a very expensive and bulky. That's why, a low cost, small size sensor to monitor on-line the type and quality of specific tested gas would be of great interest, especially for companies, where acquiring a GC/MS system is out of question.

One of the ideas proposed for improvement of selectivity in small size gas sensors is use of different metal wires [2], semiconductor oxides nanoarchitectures [3], etc. Another opportunity is to develop gas sensors based on ZnO nanorods, SnO_2 and In_2O_3 nanowires, which showed resonable response and recover characteristics [2-5] and can potentially overcome obstacles of other type of sensors, such as sensitivity, selectivity, etc. Among different nanomaterials nano-ZnO is one of the most promising multifunctional materials for gas sensors [3,6]. In this context, ZnO nanorods have advantages of large surface area, mechanical and thermal stability [3-6], thus possibility to be selective/sensitive and work in harsh environments. The physical properties of the nano-ZnO materials depend on the microstructure, including morphology, crystal size, orientation, aspect ratio and crystalline density [6,7]. Sensing properties of nano-ZnO are directly related to its preparation history, particle size, surface to volume ratio, morphology and operating temperature. The signal consists of conductivity changes due to gas adsorption on the surface and permits to detect real-time events.

Recently, the use of single ZnO nanorod and branched nanorods as low-dimensional building blocks-functional units in nanosensors and nanodevices were demonstrated [3,4]. Tien et.al. [7] also demonstrated a current response of a factor ~3 larger for Pt-coated multiple ZnO nanorods versus ZnO thin films upon exposure to 500 ppm H_2 in N_2 at room temperature. According to Tien et.al [7] the ZnO multiple nanorods sensors showed a faster response and a slower recovery in air after H_2 exposure than ZnO film films. Also have been presented single nanowires of different metal oxides and metal catalyst coatings(Pd, Pd, Au, Ag, Ti and Ni) on multiple ZnO nanorods [8], which are easy to fabricate and possess enhanced sensing properties. A limitation is that size must be tailored to accommodate to low-concentration of interest.

In this work we have focused on using in-situ lift-out technique in focused ion beam (FIB) system to fabricate individual silver-doped ZnO nanorod-based nanosensor with two electrodes to selective detect hydrogen at room temperature.

2. EXPERIMENTAL DETAILS

Slices of a *p*-type silicon or glass were used as a substrate for the fabrication of the ZnO nanorods. Si substrates were cleaned with acetone:ethanol (50:50) mixture in an ultrasonic bath and etched by piranha solution (2:1 mixture of concentrated H_2SO_4/30%H_2O_2) at room temperature for 25 min. In a typical procedure, samples was prepared using 0.1-0.5 M of zinc sulfate and 0.001-0.005 M of silver sulfate $Ag_2(SO_4)$ (99.5%) which was dissolved in 100 ml DI–water. An ammonia solution (29.6%) was added which immediately started a heterogeneous reaction. The vessels is placed on a preheated oven for 20 min at 95 °C and then allowed to cool down to room temperature for 30 min [9]. After the reaction was completed the grown ZnO nanorods on the substrates were rinsed in deionized water for 2 min and then the samples were dried in air at 150 °C for 5 min. Manipulation and reactions were inside a fumehood.

The samples with pure and doped ZnO nanorods were analyzed by X-ray diffraction (XRD) using a Rigaku 'DB/MAX' powder diffractometer, Cu K_α radiation source (λ=1.54178 Å), a scanning rate of 0.02°/s in the 2θ range from 10 to 90°. The size and morphology of the samples with ZnO nanorods were observed with a JEOL scanning electron microscope (SEM). The composition of ZnO nanorods was carried out using the Energy dispersive X-ray spectroscopy (EDX), in combination with SEM.

Information on local vibrational modes in doped ZnO nanorods was obtained from Raman backscattering experiments in a conventional micro-Raman setup Horiba Jobin Yvon LabRam IR spectrometer with a charge-coupled detector (CCD). The X-ray photoelectron spectroscopy (XPS) measurements were conducted in the analysis chamber equipped with a hemispherical electron energy analyzer (Phoibos 100, SPECS GmbH) and a dual-anode (Al Kα, 1486.6 eV and Ag Lα, 2984.4 eV) monochromatic X-ray source (XR50M, SPECS GmbH). The different characterization techniques confirmed that the nanorods are highly crystalline with regular rods distributed throughout the substrate surface.

3. RESULTS AND DISCUTIONS

Figure 1 shows the XRD patterns of silver-doped ZnO nanorods, which demonstrates that the all ZnO nanorods are with wurtzite structure. It can be seen that all diffraction peaks are caused by crystalline ZnO with the hexagonal wurtzite structure (space group: $P6_3mc$(186); a = 0.3249 nm, c = 0.5206 nm). The data are in agreement with the Joint Committee on Powder Diffraction Standards (JCPDS) card for ZnO (JCPDS 036-1451) [10]. It should be pointed out that the substance phase of silver was found, which is possible because of content of metal. No characteristic peaks of impurity phases such as Zn, S or $Zn(OH)_2$ and no diffraction peaks except ZnO were found, which indicates that only single-phase hexagonal ZnO is present. This means that the impurity does not change the wurtzite structure of ZnO.

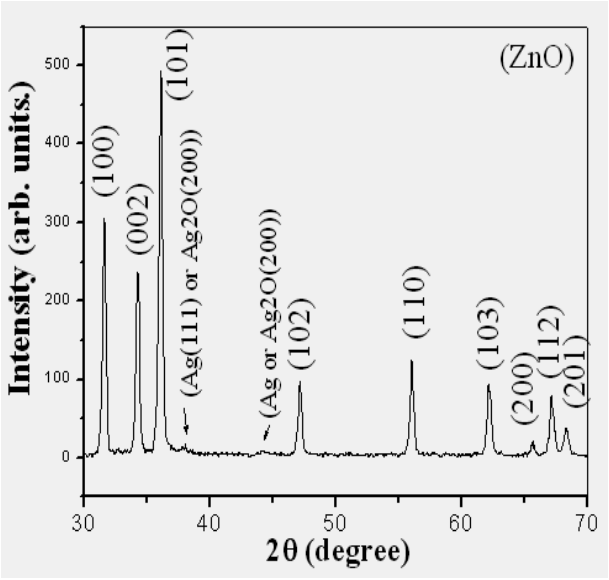

Figure 1. The XRD pattern of the ZnO nanorods.

In order to examine the surface morphology and for measurement of the rod sizes, SEM has been used. The ionic radius of Ag and Zn in the wurtzite ZnO crystals are $r(Ag^{1+}) = 0.126nm$, and $r(Zn^{2+}) = 0.074nm$, respectively. The lattice deformation was observed for Ag doping due to its bigger ionic radius. From SEM images we could not detect changes for doped samples. However, from the values from the Scherrer formula we observed changes which indicate that the lattice deformation depends on the ionic radius of doped elements in ZnO nanorods. Using energy dispersion X-ray spectroscopy, we found that the Zn:O ratios in our nanostructures to be 1:1 atomic ratio in all samples. Ag was determined as 3at% in ZnO material by using XPS. The EDX spectra of these samples indicate that the positions of the peaks O-K$_\alpha$, Zn-L$_\alpha$, and Ag-L$_\alpha$ appeared at 0.817, 1.109 and 2.983 keV, respectively. The quality of the grown ZnO rods is demonstrated by the stoichiometric

composition deduced from the EDX analysis as well as by the XRD crystallographic data.

Chemical characterization - X-ray photoelectron spectroscopy (XPS) was used to monitor changes in the chemical composition of the nanorods-based structure. Observed XPS peaks at ~1022.5 eV and ~1045.5 eV correspond to the $2p_{3/2}$ and $2p_{1/2}$ core levels of Zn in ZnO (not shown). No significant changes in the Zn-2p core levels were found for the pure ZnO samples. All samples show a clear photoelectron peak at ~ 531.2 eV, corresponding to the O 1s core level in ZnO.

Typical SEM images of the silver- doped ZnO nanorod are shown in Fig. 2. The lengths of ZnO nanorods are about 5-10 μm. According to our experimental results, the nanorods obtained by our process can be easily transferred to other substrates and handled by FIB fabrication of nanodevices [3,4,9].

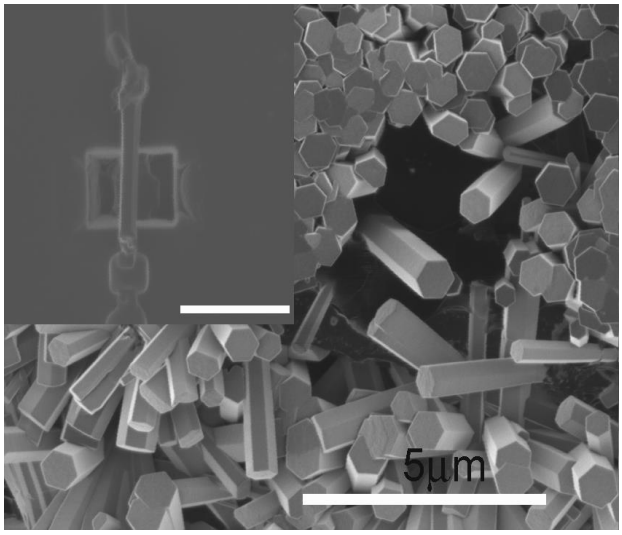

Figure 2. SEM images of silver-doped ZnO nanorods. Inset show an individual nanorod-based sensor fabricated by nanolithography in focused ion beam system. Scale bar is 5 μm.

Inset in Figure 2 demonstrate an individual nanorod-based sensor fabricated by nanolithography in focused ion beam system. The typical time taken to perform this in-situ lift-out FIB nanofabrication is 20 min. Also taken in the account that nanorod synthesis was done in 10 min, we contribute to overcome some obstacles in use of nanorods /nanowires for sensor production. At the same time, we satisfied the features of the nanowire synthesis method desired for industry like low-cost materials and processings, control of process parameters, environment friendly reagents, etc.

4. GAS SENSITIVITY/SELECTIVITY MEASUREMENTS

The sensor test chamber is a plastic container with a sample volume of 100 ccm. Clip leads connect the sensor to a 1-5 Vdc power supply and analog input of the data acquisition system. Gas mixtures are supplied to the chamber by two mass flow controllers, which are controlled by settings in the LabView program. Sensor and ambient temperatures are recorded automatically by resistance temperature detectors. Test parameters such as concentration, gas flow rates, length of test, number of test cycles, and sampling rate can be input through the user interface and stored for future use. At the end of a test, data files are automatically stored on the test computer. After the exposure to hydrogen gas (or other test gas) sensor were maintained for a recovering period in dry air.

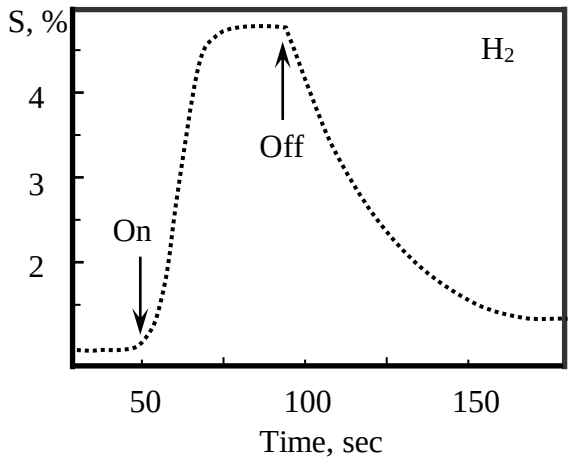

Figure 3. Gas sensitivity of single nanorod-based sensor.

The room temperature sensitivity of the single nanorod ZnO nanosensor to 200 ppm H_2 is shown in Figure 3. The sensitivity $S=\Delta R/R$ ~4,7 % of our sensor is attractive for further investigation for practical H_2 sensor applications. We found that our single silver-doped ZnO nanorod sensor has a gas sensitivity of less than 0.5% for O_2, CH_4, CO, ethanol and LPG under the same conditions.

A typical curve of sensitivity to different gasses of sensor is presented in Figure 4(a,b). Here can be observed that sensitivity of the silver-doped zinc oxide sensor element measured against CH_4 gas concentration at 20°C (Fig.4a). The linear detection range was obtained for nanosensor up to 0.2% of sensitivity. These results ensure application of this novel sensor as an selective one to develop a sensor to detect H_2 at low ppm range (100-200 ppm) at room temperature.

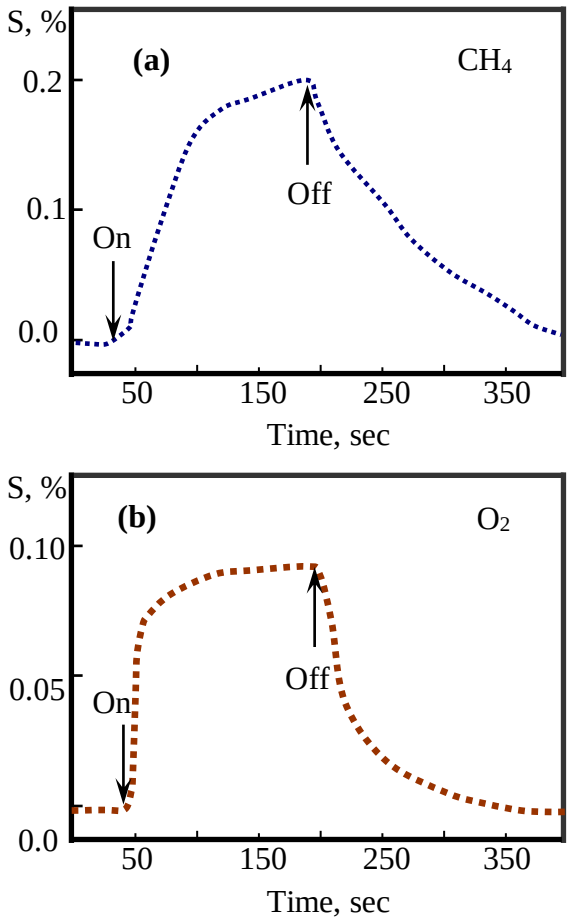

Figure 4. Gas sensitivity of single nanorod-based sensor to (a) CH_4 and (b) O_2 gases at room temperature.

4. CONCLUSION

In summary, ZnO 1-D nanorod structures were synthesized through a novel hydrothermal route without template. The architectures are constructed of high-quality ZnO 1-D nanorods of 100 nm in radius and 5-10 μm in length. X-ray diffraction, energy dispersion X-ray spectroscopy, scanning electron microscopy, micro-Raman spectroscopy measurements have been used to characterize the samples. These characterizations reveal that the ZnO architectures are hexagonal faced nanorods with good crystal quality.

The typical time taken to perform this in-situ lift-out FIB nanofabrication is 20 min. Also taken in the account that nanorod synthesis was done in 10 min, we contribute to overcome some obstacles and conception that nanorods/nanowires are not convenient for sensor production. At the same time we satisfied the features of the nanowire synthesis method desired for industry are low-cost materials as processing, control of process parameters, environment friendly reagents, etc.

Further work: Our further research efforts are directed towards synthesizing oriented one – dimentional nanorods, which will facilitate construction of semiconductor nanodevices with well-ordered alignment, which are extremely important for scientific, technological and industrial application. Development of single doped ZnO nanorod sensor for biosensing.

Acknowledgements. The research described in this publication was made possible in part by an Award No. MTFP-1014B Follow-on of the Moldovan Research and Development Association (MRDA) under funding from the U.S. Civilian Research & Development Foundation (CRDF). We acknowledge the financial support by the RFFI Project 036/R from the Ministry of Education and Science of Moldova and from Supreme Council for Research and Technological Development of the Academy of Sciences of Moldova.

References

1. Bucheli Th. D., Brändli R. C., *Journal of Chromatography 1110(1-2) p. 156, 2006.*

2. E. C. Walter, R. M. Penner, H. Liu, K. H. Ng, M. P. Zach, F. Favier, *Sensors from electrodeposited metal nanowires, Surface and Interface Analysis, 34(1), pp. 409 - 412, 2002.*

3. O. Lupan, G. Chai, L. Chow, *Microelectron. J., 38 p. 1211 2007.*

4. O. Lupan, G. Chai, L. Chow, *Microelectron. Eng. (2008), doi:10.1016/j.mee.2008.06.021.*

5. A. Ohtomo, M. Kawasaki, Y. Sakurai, I. Ohkubo, R. Shiroki, Y. Yoshida, T. Yasuda, Y. Segawa, and H. Koinuma, *Mater. Sci. Eng. B 56, p. 263 1998.*

6. Ü. Özgür, Ya. I. Alivov, C. Liu, A. Teke, M. A. Reshchikov, S. Dogan, V. Avrutin, S. J. Cho, H. A. Morkoç*, J. Appl. Phys., 98, p. 041301, 2005.*

7. L.C. Tien, P.W. Sadik, D.P. Norton, L.F. Voss, S.J. Pearton, H.T. Wang, B.S. Kang, F. Ren, J. Jun, J. Lin, *Hydrogen sensing at room temperature with Pt-coated ZnO thin films and nanorods, Appl. Phys. Lett. 87 p. 222106-222108, 2005.*

8. C.S. Rout, G.U. Kulkarni, C.N.R. Rao, *Room temperature hydrogen and hydrocarbon sensors based on single nanowires of metal oxides, J. Phys. D: Appl. Phys. 40 pp. 2777-2782, 2007.*

9. O. Lupan, L. Chow, G. Chai, B. Roldan, A. Naitabdi, A. Schulte, H. Heinrich, *Nanofabrication and characterization of ZnO nanorod arrays, Materials Science and Engineering, B 145 p. 57, 2007.*

10. JCPDS PDF Card 036-1451.

Recomandat spre publicare 06.09.2008